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TECHNICAL PROGRESS REVIEWS

# REACTOR FUEL PROCESSING

Prepared for U. S. ATOMIC ENERGY COMMISSION by ARGONNE NATIONAL LABORATORY

OCTOBER 1958

VOLUME 1

NUMBER 4

## TECHNICAL PROGRESS REVIEWS

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# REACTOR FUEL PROCESSING

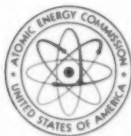
*a review of recent developments prepared by*

ARGONNE NATIONAL LABORATORY

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## *foreword*

This quarterly review of *Reactor Fuel Processing* has been prepared at the request of the U. S. Atomic Energy Commission. It is the fourth issue of this series, intended to assist those interested in keeping abreast of important developments in this field. In each review it is planned to cover those particular subjects in which significant new results have been obtained. The review does not purport to abstract all the literature published on this broad field during the quarter. Instead it is intended to bring each subject up to date as circumstances warrant.

Interpretation of results, where given, represents the opinions of the editors who are personnel of Argonne National Laboratory, Chemical Engineering Division. The reader is urged to consult the original references for more complete information on the subject reported and for the interpretation of results by the original authors.

S. LAWROSKI

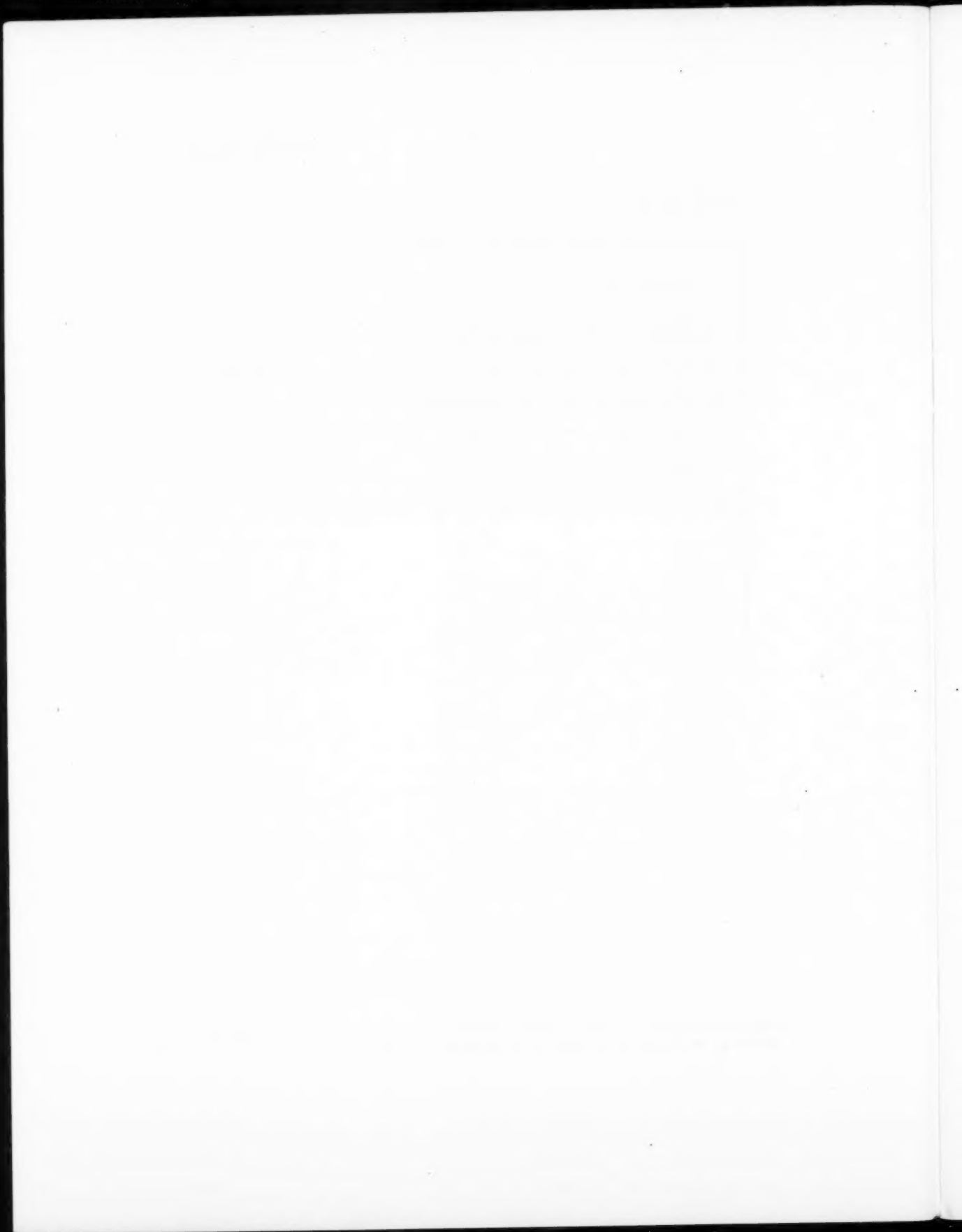
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# REACTOR FUEL PROCESSING

## COMMERCIAL ASPECTS OF FUEL REPROCESSING

Four members of the staff of the Reactor Development Division, USAEC, have reviewed the current AEC fuel-cycle program.<sup>1</sup> The objectives of the program are to develop more efficient fuels for reactors using  $U^{233}$ ,  $U^{235}$ , natural uranium, and plutonium; to utilize these fuels at elevated temperatures; to increase burn-up; and to develop fabrication techniques and manufacturing processes to lower the unit cost of producing fuel elements. To achieve these objectives, it is hoped to emphasize the three areas of operation: (1) fundamental engineering research and development on fissionable and fertile structural materials that may be efficiently utilized in the fabrication and manufacturing of less expensive fuel assemblies; (2) design and fabrication of prototype fuel elements having improved resistance to radiation and longer life at elevated temperatures, such elements to be tested extensively in operating reactors; and (3) based on successful performance of these prototype fuel elements, full or partial core loadings will be tested in power reactors under normal operating conditions. These programs will be carried out both by industrial concerns and AEC laboratories. The AEC program will include a major effort on oxides, carbides, and other ceramic or cermet materials containing uranium, thorium, and plutonium. Work will be aimed primarily toward lower fabrication materials costs and longer lifetime of fuels suitable for full-scale power reactors.

The expanded program for fuel-cycle development requires that increased effort be devoted to chemical processing development. The emphasis on oxides, carbides, and other ceramics

and cermets necessitates expansion of the work already begun on these materials. Increased effort will be placed on volatility work and on the application of pyrometallurgical process development now under way. In keeping with the goal of lowered fuel-cycle costs, increased effort will be devoted to developing waste-treatment methods.

As a part of a survey entitled "Fuel for the World's Reactors," the August 1958 issue of *Nucleonics* lists considerable information concerning the uranium and thorium conversion services of six U. S. companies and the fuel fabrication services, experiences, and capabilities of 19 U. S. companies.<sup>2</sup>

The effect of uranium recycle on transuranic element build-up has been calculated by Arnold.<sup>3</sup> Data are present for  $U^{236}$ ,  $U^{237}$ ,  $Np^{237}$ , and  $Pu^{238}$  as a function of irradiation level, number of cycles, enrichment, and the removal of a portion of the  $U^{236}$  in a gaseous-diffusion plant. An important conclusion is that all the recycle problems due to isotope build-up may be reduced by an order of magnitude by the removal of 25 per cent of the  $U^{236}$  in a gaseous-diffusion plant.

### References

1. R. C. Dalzell et al., AEC's Fuel Program, *Nucleonics*, 16(8): 78 (August 1958).
2. A Nucleonics Survey of Fuel Converters and Fabricators, *Nucleonics*, 16(8): 101-104 (August 1958).
3. E. D. Arnold, Effect of Uranium Recycle on Transuranic Element Build-up, *Nuclear Science and Engineering*, 3: 707-725 (June 1958).

## FUEL REPROCESSING FEATURES OF U.S.-EURATOM PROGRAM

As a part of the proposed joint U.S.-Euratom program which has been submitted to Congress, the United States proposes to reprocess fuels provided by the United States to users in the Euratom countries. Some of the more important details concerning this proposed activity are as follows.<sup>1</sup>

*Charges.* The draft Agreement for Cooperation says that such reprocessing will be performed at established U. S. domestic prices in effect upon delivery of such material.<sup>2</sup>

*Duration.* A working paper included with the proposal says that the United States will be prepared to perform reprocessing services "until such time as a suitable processing plant is constructed in Europe," and notes that "there may be an economic advantage in waiting until the power reactor capacity has reached several million kilowatts before building such a plant."

*U. S. Technical Aid.* The USAEC "will be prepared to provide technical advice and assistance, as desired, in the design and construction of the Eurochemic pilot plant, to be built under Organization for European Economic Co-Operation (OEEC) auspices at Mol, Belgium, and in the design and construction of any future large-scale chemical processing plant that the European Atomic Energy Community decides to construct."

Also among key provisions in the Euratom package sent to Congress last month are those having to do with the disposition of the special nuclear materials, including  $U^{235}$  and plutonium, that are recoverable from irradiated fuels obtained initially from the United States. The more important details concerning this subject are as follows:

*Disposition.* The Agreement for Cooperation provides that Euratom may keep, subject to the proviso that they may be used only for peaceful purposes, any of the materials, including  $U^{235}$  and plutonium, extracted from fuel initially purchased from the United States. This applies whether or not the fuel is processed in the United States or Europe. With respect to such materials which are in excess of Euratom's

needs, the Agreement says that "the International Atomic Energy Agency (IAEA) is granted the right of first option to purchase them at the announced fuel value price in effect in the United States at the time of purchase." The Agreement then goes on to say that "in the event this option is not exercised by the IAEA, the U. S. Government is prepared to purchase such materials at the U. S. announced fuel value price in effect at the time of purchase."

*Plutonium Quantity Limitation.* The USAEC would be authorized "to acquire from the Community up to 4100 kg of plutonium for use only for peaceful purposes."

*Plutonium Time Limitation.* No contract to purchase plutonium from reactors included in the joint program "shall be for a period greater than 10 years of operation of such reactors or December 31, 1973, whichever is earlier."

*Plutonium Purchase Price.* The funding summary included in the Euratom package says that "the expenditures required to cover repurchase of all plutonium estimated to be recovered from reprocessed spent fuel from (the joint program) during the 10 year period" would amount to \$50 million. This, considering the 4100 kg authorized to be purchased, gives a per-gram price for the plutonium of \$12.

*$U^{235}$  Provisos.* The only limitations on U. S. purchase of  $U^{235}$  in irradiated Euratom fuels is that the quantity should not exceed the total quantity provided initially by the United States less burn-up; that no purchase commitments should be made beyond the lifetime of the Agreement for Cooperation, which is 25 years; and that the price should not exceed the domestic published price schedule.

*Fuel Guarantee Rationale.* Of all the provisions of the Euratom package sent to Congress in June, probably the most controversial and least understood are those having to do with an intricate system of fuel-cycle guarantees designed to assure that reactor fuel costs will be kept within low enough limits to retain the interest and participation of European utilities in the U.S.-Euratom power program. In various

working papers provided to the Congress last month, the method by which they were arrived at emerges as follows:

1. If the power plants in the one million kilowatt program range in cost from \$250 to \$350 per installed kilowatt, as estimated, then these capital costs under the financing scheme envisioned (part low interest government loan, part normal financing, giving an over-all interest rate of about 6 per cent) will amount to about 5.5 to 7.7 mills per kilowatt hour. This compares with capital costs for an equivalent coal-burning facility of about 3.1 mills per kilowatt hour.

2. The total average cost of power from coal in the Euratom countries is now about 10.9 mills per kilowatt hour.

3. If, in the light of this cost of power from coal, European utilities are to be interested in experimenting with nuclear power at this time, then the fuel costs of nuclear power must be held to a sufficiently low level to counterbalance, in part at least, the comparatively high capital costs involved. In this connection it is felt by the U.S.-Euratom negotiators that the interest of European utilities can be retained if fuel costs for the nuclear plants in the million kilowatt program could be held to 4.2 mills per kilowatt hour, giving over-all nuclear power costs of about 11.7 to 13.9 mills, including an allowance of 2.0 mills per kilowatt hour for operation and maintenance. (The theory here is that nuclear power can be allowed to cost a little more at first because, during the life of the nuclear power plants, nuclear fuel costs will probably substantially diminish while conventional fuel costs will rise, thus canceling out uranium's initial disadvantage.)

4. It is felt by the U.S.-Euratom negotiators that this fuel-cycle cost of 4.2 mills per kilo-

watt hour can be achieved if the following breakdown of costs can be achieved.

	Mills
Fuel inventory	0.6
U <sup>235</sup> burn-up	2.3
Fabrication	1.5
Chemical processing	0.3
Conversion of UNH to UF <sub>6</sub>	0.1
Transport and insurance	0.3
Total	5.1
Plutonium credit	0.9
Net total	4.2

In this breakdown the plutonium credit was figured at \$12 per gram less \$1.50 per gram to cover conversion of plutonium nitrate to plutonium metal, including losses.

5. It is felt, in turn, by the negotiators, as explained in their working papers, that the above breakdown of fuel-cycle costs is achievable if uranium dioxide fuel elements between 0.25 and 0.50 in. in diameter and enriched up to 3 per cent in U<sup>235</sup> cost no more than \$100 per kilogram of contained uranium if clad in stainless steel and no more than \$140 per kilogram of contained uranium if clad in zirconium and if the buyer is assured an irradiation level of 10,000 Mwd per ton.

## References

1. *The Forum Memo to Members*, Atomic Industrial Forum, Inc., Vol. 5, No. 7, July 1958.
2. *Reactor Fuel Processing*, Vol. 1, No. 1, February 1958. (Available from Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C.)

## PREPARATION FOR FUEL REPROCESSING

There continues to be great interest in the development of mechanical and chemical methods for decladding and dissolving the wide variety of power reactor fuels which are under consideration.

### *Mechanical Disassembly*

For many of the proposed fuels it would be desirable to be able to remove the cladding material mechanically. Studies have continued on the use of various types of saw blades. Tests on the cutting of simulated fuel elements<sup>1</sup> (ceramic-filled stainless-steel tube bundles and carbon-steel stacked plate assemblies) show that both circular sawing (with friction and diamond blades) and shearing (by alligator and either mechanical or air-operated guillotines) are mechanically feasible. It is also indicated<sup>2</sup> that diamond blades and U-tooth blades would give satisfactory service in the cutting of simulated fuels. In life tests the U-tooth friction blade has made more than 400 cuts of simulated fuel elements (each element consists of a bundle of nine  $\frac{1}{2}$ -in.-diameter stainless-steel tubes filled with a ceramic stand-in for  $\text{UO}_2$ ) without excessive blade wear. In similar tests diamond blades have demonstrated satisfactory performance for greater than 200 cuts. Tests on the diamond blade were discontinued after 200 cuts, but inspection at that time revealed very little wearing (approximately 6 mils) on the cutting surface of the blade.

Tests were run at the Williams Patent Crusher & Pulverizer Co. plant in St. Louis on a pulverizer being evaluated for use in mechanically disintegrating fuel elements. These tests showed that simulated fuel elements could be reduced to steel shrapnel (roughly  $\frac{1}{2}$  by  $\frac{1}{2}$  in.) and fragmented powder in such a mill. However, they also indicated that fuel elements should be first reduced in size to approximately 25-lb pieces to permit efficient operation of the pulverizer.

### *Chemical Processing*

There are a number of processes under consideration for chemical dissolution of fuel elements. Some of these processes remove the clad separately; some dissolve both clad and fuel together.

#### *Nitric Acid Dissolution*

Dissolution rates for uranium in a 5-in.-diameter continuous dissolver were determined with a product purity as low as 0.05 mole nitric acid per mole of uranium.<sup>1</sup> It was noted that the dissolution rate of depleted uranium slugs used for these studies was up to 50 per cent greater than the dissolution rate of normal uranium slugs. The depleted slugs had been reduced with a commercial grade of magnesium rather than with the highly purified magnesium used for the normal uranium slugs.

Initial rates of dissolution for  $\text{UO}_2$  as low as 0.1 and 0.4 g/(hr)(sq cm) were observed in boiling 8M and 12M nitric acid,<sup>2</sup> respectively. As nonuniform attack resulted in increasing the surface area, the reaction rate increased with time. Acid consumption to terminal acidities greater than 2.4 molar nitric acid was in the range of 2.4 to 2.8 moles of nitric acid per mole of  $\text{UO}_2$  dissolved.

The effect of chemical additives on the dissolution of uranium in nitric acid is being studied<sup>1</sup> in an attempt to shorten dissolution time cycles for dingot (direct ingot) uranium. Dissolution rates for dingot uranium in 6M  $\text{HNO}_3$ -1M UNH were not appreciably affected by the addition of sulfuric acid in concentrations up to 0.05M. At 0.1M  $\text{H}_2\text{SO}_4$  the rate was increased by factors from 1.3 to 1.8 over that without sulfuric acid. However, these latter rates are still only about half those observed for ingot metal in the absence of sulfuric acid.

Attempts to relate dissolution rate of dingot uranium to grain size and impurity content were continued. Dissolution rates in 8M  $\text{HNO}_3$  were



not significantly different for samples of dingot metal having a macroscopic grain size difference of about five. A series of centrifugally cast uranium base-carbon-silicon alloys prepared from dingot uranium showed dissolution rates in 8M  $\text{HNO}_3$  ranging from one to seven times that of production dingot uranium. Dissolution rate could not be related to silicon content, carbon content, or the silicon/carbon ratio.

Small concentrations of  $(\text{NH}_4)_2\text{SiF}_6$  markedly increase the instantaneous dissolution rates of both ingot and dingot metal in  $\text{HNO}_3$ -UNH solutions.<sup>2</sup> The dissolution rate of dingot metal in 1.0M to 6.0M  $\text{HNO}_3$ , 1.0M UNH, and 0.005M to 0.0075M  $(\text{NH}_4)_2\text{SiF}_6$  solutions at boiling temperatures equals or exceeds the rate for ingot metal in the absence of added  $(\text{NH}_4)_2\text{SiF}_6$ . The effects of these concentrations of  $(\text{NH}_4)_2\text{SiF}_6$  on stainless-steel corrosion and solvent-extraction performance are under investigation.

End-grain attack of nitric acid on uranium metal has been shown to be a result of both fabrication methods and the presence of carbon in the metal. Two dingot uranium alloys were alpha-rolled (640°C) to about 75 per cent reduction in cross-sectional area and beta heat-treated (730°C for 15 min, water-quenched). One alloy contained 284 and 1360, and the other 1103 and 110 ppm carbon and silicon, respectively. The low carbon alloy exhibited only moderate end-grain attack, whereas the high carbon alloy experienced severe end-grain attack. Only moderate end-grain attack occurred on the high carbon alloy in the as-cast condition. However, the dissolution rate of both alloys was greater in the as-cast plus beta heat-treated condition than in the alpha-rolled plus beta heat-treated condition; i.e., the absence of end-grain attack was associated with an increase in dissolution rate.

### Dissolution of Alloyed Fuels

The incorporation of such materials as stainless steel, zirconium, niobium, molybdenum, and silicon in fuel alloys necessitates the use of corrosive dissolving media, for example, hydrofluoric acid, sulfuric acid, and dilute aqua regia. Two of the processes receiving the most attention at the present time are called "Darex" and "Zirflex." A meeting was held at Idaho Falls on July 29 and 30, 1958 to discuss these processes. In attendance were representatives

of the Idaho Chemical Processing Plant (ICPP), Hanford, Oak Ridge, Savannah River, Brookhaven, and Argonne. Much of the material reported herein on these two subjects was obtained at that meeting.

*Darex.* A flow sheet of the Darex process was given in the first review of this series.<sup>3</sup>

As presently conceived for uranium-stainless-steel alloys (APPR-1), 6.7 kg of alloy is to be dissolved in 100 liters of 5M  $\text{HNO}_3$ -2M HCl. After dissolution is complete, the volume is reduced to 50 liters. Then 100 liters of 16M  $\text{HNO}_3$  is added to the concentrated solution, and the solution is again reduced to 50 liters. Fifty liters of water is added to produce 100 liters of feed solution with the following composition.

0.5 kg U	} in 3M HNO <sub>3</sub> containing
6.2 kg S.S.	

For such a procedure it has been determined that 3 moles of hydrogen ion, 0.2 moles chloride ion, and 0.9 mole nitrate ion are lost per mole of metal dissolved. This procedure, as indicated, makes use of a batch boildown for chloride ion removal.

Dissolution studies have also been made on prototype material for the Yankee Atomic Electric fuel, which is  $\text{UO}_2$  with a stainless-steel clad. In this case it was found that 4 moles of hydrogen ion were consumed per mole of material dissolved. Experience has indicated the need for a condenser with 2M hydrochloric acid because, with 1.7M hydrochloric acid, the metal becomes passivated at 80 per cent dissolution. The distilled acids are recovered with a stripping and rectifying column.

Small-scale continuous dissolution studies<sup>4</sup> were made on Yankee fuel using 5M  $\text{HNO}_3$ -1M HCl. The dissolver product varied in uranium concentration from 112 to 144 g/liter. Batch chloride removal tests on simulated dissolver solution indicated that specification (30 ppm of chloride) solvent-extraction feed could be made by 50 per cent evaporation of the dissolver product, addition of an equal volume of 70 per cent  $\text{HNO}_3$ , evaporation to a boiling point of 126°C, and dilution to the original volume.

The following observations have been made during continuous dissolution and chloride removal:

1. Chloride ion apparently is more readily volatilized from solutions with high uranium concentrations.

2. A coating of silica appears in the stripping tower. This coating of silica may be removed with hot caustic.

3. Titanium is a very good material of construction, especially with aqua regia solutions.

Equipment for continuous operation has been built at Oak Ridge National Laboratory (ORNL) and is now running cold. It has been operated for extended runs with Army Package Power Reactor (APPR) fuel elements. The materials of construction for the various units are as follows:

Dissolver: Titanium

Stripper: Glass

Nitric acid boiler: Glass-lined stainless steel

Feed adjustment: Stainless steel, but titanium is preferred

The ICPP also has a pilot unit. The dissolver is made of titanium, and it is equipped with a down-draft glass condenser.

In order to predict the stability of various Darex feed solutions to precipitation, a series of solutions were prepared at Hanford and allowed to stand at room temperature for one week. The solutions were seeded and the appearance of precipitates noted. The range of concentration studies was as follows:

Uranium stainless steel ratio	0.5 to 5
UNH (M/L)	0.5 to 2
HNO <sub>3</sub> (M/L)	0 to 7

The following general observations may be made:

1. At high total salt and high nitric acid concentration, the solutions were unstable.

2. At intermediate stainless steel and intermediate uranyl nitrate and high acid concentrations, the solutions were unstable.

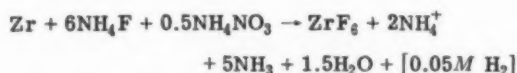
3. At low stainless steel and low uranyl nitrate concentrations, the solutions were stable.

When extracted with 30 per cent TBP in a hydrocarbon, the distribution coefficient was as expected (0.8 to 6) for Purex type extraction. With a low acidity the stainless-steel salts exerted some salting into the organic phase which was overridden at high nitric acid concentrations. The decontamination from stainless-steel

products was excellent in batch extraction and stripping.

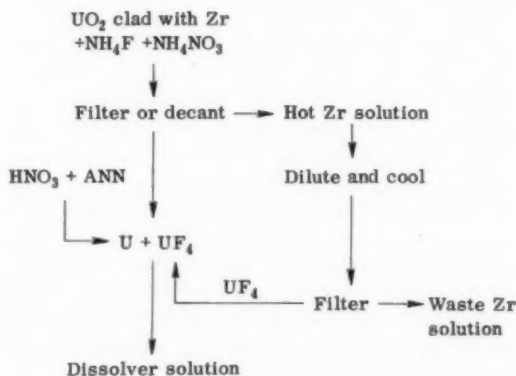
For low acid systems, feed solutions were found which were stable at zero nitric acid. Some solutions were stable with added sodium hydroxide, but no stable solution was found with a pH greater than 6.

*Zirflex.* This process calls for the dissolution of zirconium or Zircaloy-clad UO<sub>2</sub> fuel elements in ammonium fluoride. The two dissolution reactions may be written as follows:



The presence of the nitrate ion not only depresses the formation of hydrogen but it aids in the dissolution of the tin present in the Zircaloy. During the dissolution, it is important to remove ammonia since its presence results in a slower reaction rate.

The flow sheet is conceived as follows:



The following points may be made of the ammonium fluoride dissolution studies:

1. The dissolution rate increases as the free fluoride concentration increases. (The free fluoride concentration is defined as the fluoride concentration minus six times the zirconium concentration.)

2. The zirconium solubility decreases as the free fluoride concentration increases.

3. With decreasing free fluoride concentrations, the uranium solubility decreases. How-



ever, at the same time, the dissolution rate decreases.

Zirconium exposed to high temperature water develops an oxide film which is quite tenacious. Ammonium fluoride does not react readily with oxide film. A solution of ammonium fluoride in hydrofluoric acid with the composition  $\text{NH}_4\text{F} \cdot 2.2\text{HF}$  reacts well with the oxide film and dissolves it.

Some pilot-plant work has been done on this process at Hanford. In the dissolution of 3 to 4 kg of zirconium in 20 liters of solution, dissolution curves showing 70 per cent dissolved in 40 min and 95 per cent dissolved in 100 min have been obtained. Under the same conditions, oxidized material dissolves at a rate such that only 5 per cent is dissolved in 40 min. A molten salt step results in the removal of most of the oxide film in 12 hr. Uranium losses were about 0.05 per cent in solution.

The effect of dissolved uranium(IV) on rate of attack of sintered  $\text{UO}_2$  by  $6\text{M NH}_4\text{F}-0.5\text{M NH}_4\text{NO}_3$  was studied.<sup>2</sup> The rate is lower by a factor of about 10 when the solution is saturated with uranium(IV). This indicates that less  $\text{UO}_2$  core material should convert to the uranium(IV) fluoride during the Zircaloy-2 decladding operation than was estimated previously from results of experiments with uranium metal.

A sample of 1.5 per cent plutonium-aluminum alloy<sup>5</sup> was exposed to boiling  $6\text{M NH}_4\text{F}$  for 6 hr. The reaction was vigorous at first but subsided after a few minutes, presumably because of the formation of a protective white coating on the alloy. After 15 min of exposure the supernatant solution contained 2.1 mg/liter of plutonium, which decreased over the 6-hr digestion period to about 1 mg/liter. The supernatant also contained a suspended white solid, which was soluble in nitric acid but apparently contained no plutonium.

The maximum observed solubility of 2.1 ml/liter of plutonium was applied to the decladding of a plutonium-aluminum alloy fuel rod (1.5 wt.% plutonium-aluminum cylinder 9 ft long by 0.5 in. in diameter, clad in 0.030 in. of Zircaloy-2 and capped with 0.5 in. of Zircaloy-2). The plutonium loss to the decladding solution was estimated to be 0.1 per cent. Thus it is believed that the Zirflex process can be applied to the decladding of plutonium-aluminum alloy fuels.

### Dissolution of Zirconium and Stainless Steel in $\text{HNO}_3\text{-HF}$

The use of mixtures of  $\text{HNO}_3$  and HF are under study at several sites as dissolving media for zirconium and stainless steel.

Hanford results indicate that type 304C stainless steel may be dissolved in  $\text{HNO}_3\text{-HF}$  with the following results:

$\text{HNO}_3$ M/L	HF M/L	Dissolution rate mils/hr
0.5	0.5	2.8
	1.0	8.0
	2.0	11.8

Hastelloy F is used to contain the reaction. The corrosion rate is 20 to 30 mils/month.

The ICPP is considering  $\text{HNO}_3\text{-HF}$  mixtures for the dissolution of 98 per cent uranium-2 per cent zirconium alloys. The zirconium dissolution rate in  $\text{HNO}_3\text{-HF}$  is dependent on the HF concentration. The nitric acid concentration at a constant HF concentration does not affect the dissolution rate at  $40^\circ\text{C}$ .

The solubility of  $\text{ZrF}_4$  is  $<1$  g/liter in 13M nitric acid. This solubility falls off quite rapidly with increasing nitric acid concentration. Also, at high nitric acid concentrations, the solubility of  $\text{ZrF}_4$  appears to be temperature independent. With these  $\text{HNO}_3\text{-HF}$  solutions, the reaction slows down very markedly at a F/Zr ratio of 2.

Corrosion rates at  $60^\circ\text{C}$  of 6M  $\text{HNO}_3$  and 1M and 2M HF mixtures on Carpenter 20, Hastelloy F, and stainless steel 309 were 100 to 200 mils/month. Tantalum dissolved in two days. Inconel 804 gave a rate of 70 mils/month.

Oak Ridge has looked at the dissolution of  $\text{ThO}_2\text{-UO}_2$  mixtures. With 95.3 per cent  $\text{ThO}_2$ -4.7 per cent  $\text{UO}_2$ , the dissolution rate reaches a maximum in 13M nitric acid-0.4M hydrofluoric acid. The thorium nitrate in solution reduces the dissolution rate. Aluminum nitrate present at about 0.4M also decreases the dissolution rate.

With a Consolidated Edison type fuel which is  $\text{ThO}_2\text{-UO}_2$  pellets clad with stainless steel, the steel is removed with sulfuric acid. Then the oxide pellets are dissolved in a solution which is 13M  $\text{HNO}_3$ , 0.04M NaF, and 0.04M  $\text{Al}(\text{NO}_3)_3$ .

### Dissolution of Aluminum Alloys

Considerable work has been done at ICPP on dissolution of uranium-aluminum alloy fuels.<sup>6</sup>

Enriched uranium-aluminum alloy fuels are charged semicontinuously to the top of the dissolvers while acid and catalyst (mercuric nitrate), metered separately, are pumped in the bottom. Operation is thus countercurrent with the full slug bed submerged in acid or foam. Product overflows at the top of the fuel pack, and the vapors are condensed and returned to the dissolver feed stream.

The continuous dissolver has proved to be an effective device. No difficulties were experienced in operation, and the only equipment failure associated with the dissolver was the corrosion failure of the inadequately constructed catalyst feed pumps.

Control of dissolver solution concentration by variation in rate of catalyst injection into the constant acid feed stream was very successful. Only minor and infrequent adjustments in catalyst rate were required to produce constant quality feed with constant metal feed composition. The average aluminum concentration of 41 dissolver product batches collected during the earliest processing was 1.27M with extremes of 1.12M and 1.42M. The extreme values, while representing a  $\pm 12$  per cent deviation in aluminum concentration, were equivalent to a density deviation of only  $\pm 0.02$  g/cc.

In order to confirm the reliability of the extrapolation of pilot-plant data to the plant continuous dissolver, data from dissolution of extruded aluminum rod in three dissolvers were compared.<sup>6</sup> The dissolvers were the 2- and 5-in.-diameter pilot-plant dissolvers and the 7½-in.-diameter plant dissolver. All reagent feeds were 5.6M nitric acid, and all the results were normalized to 0.005M mercuric nitrate catalyst concentration. Analysis of the data from the three dissolvers indicates that there is no significant difference among the three dissolvers when rates are considered on the basis of cross-sectional area. At constant catalyst concentration (moles mercuric nitrate per liter), the dissolution rate for aluminum-uranium alloys in pilot-plant runs was proportional to the 0.8 power of the acid feed rate. In the plant dissolver the dissolution rate was proportional to the 0.77 and 0.78 power of the acid feed rate

for aluminum rod stock and unirradiated fuels, respectively. Irradiated cast alloy showed a rate dependent on the 0.7 power of the acid feed rate.

Similarly, the pilot-plant data showed that, at constant acid feed rate, the dissolution rate was proportional to the 0.33 power of the catalyst concentration (range 0.001M to 0.045M). In the plant dissolver it was shown that the dissolution rate was proportional to the 0.3 power of the catalyst concentration.

Previous work on batch dissolution had shown irradiated extruded and cast alloy dissolved significantly slower than the corresponding unirradiated material. To test this effect in the continuous dissolver, three batches of alloy fuel, each of limited burn-up range, were isolated, and each batch dissolved continuously at the same nominal aluminum dissolution rate. Catalyst was metered in each case to produce 1.2M aluminum nitrate in the dissolver product.

Burn-up does not apparently limit the dissolver capacity. Almost equivalent maximum rates were obtained with irradiated alloy as with the unirradiated alloy. However, this maximum rate was maintained with the irradiated alloy only through the use of significantly larger quantities of catalyst; i.e., 0.012M mercuric nitrate catalyst for unirradiated alloy as compared to about 0.035M catalyst for irradiated alloy.

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## RESEARCH AND DEVELOPMENT ON FUEL PROCESSING

### Solvent Extraction

#### Purex and Redox Process Improvements and Modifications

Redox and Purex are the major liquid-liquid extraction processes in use today. The Redox process employs a methylisobutylketone solvent phase, whereas the Purex solvent phase is tributyl phosphate (TBP) in a kerosene diluent. Efforts continue to improve these processes, and various modifications have been adapted to the processing of nonproduction reactor fuels.

The recycle of part of the Redox first-cycle extraction column aqueous waste stream has been demonstrated. The aqueous waste stream contains the bulk of the fission products and large amounts of aluminum nitrate. The recycle of some of the aqueous waste through the feed concentrator was demonstrated under plant operating conditions with no loss of extraction efficiency. This served to reduce considerably the amount of salting agent required, and the savings in waste-storage cost amounted to \$18 per ton of uranium processed.<sup>1</sup>

Studies are being made to adapt the Purex process to the reprocessing of nonproduction reactor fuels at Hanford.<sup>2</sup> Fuels being considered are from the Yankee, Dresden, CPPD, Piquá, Chugach, PRDC, and Northern States reactors. For reprocessing stainless-steel fuels, Hanford plans to adapt a modified Darex flow sheet in which fuel is dissolved in aqua regia and uranium is extracted with 5 per cent TBP-kerosene. It is assumed that chloride is removed by one of several head-end schemes. In a modification successfully demonstrated in batch tests, chloride was eliminated in the extraction column aqueous waste by using a scrub solution containing chromium(III) nitrate and nitric acid. The chloride was removed from the solvent phase which was 30 per cent TBP containing 5 g of fluoride ion per liter and 97 g of uranium per liter. Under these conditions the uranium strongly favored the organic phase.

#### Degradation of Purex Solvents

Purex solvent, TBP usually with a kerosene diluent, decomposes due to chemical and radiation damage to form cleavage products and polymers. These degradation products in many cases form practically unstrippable complexes with uranium and certain fission products (particularly zirconium) in the organic phase. Savannah River experience has shown extensive solvent degradation after a few months use. The rate of production of degradation products was a function of chemical environment and total radiation dosage. Nitrous and nitric acids produced degradation products in the kerosene diluent. Degradation products were firmly held in the solvent phase and were not removed by solvent washing with caustic. These degradation products were powerful extractants for zirconium in concentrations as low as 100 ppb. Zirconium once extracted was difficult to remove. Zirconium-niobium activities picked up in the extraction column were slowly released in the uranium and plutonium stripping columns. Chemical degradation was more rapid<sup>3</sup> at 70°C than at 40°C.

The principal degradation product of TBP was dibutyl phosphate (DBP). In Purex solvent at 40°C with nitric acid but no nitrous acid present, DBP was the only degradation product formed. No degradation products were formed in the kerosene diluent. When the HNO<sub>3</sub> concentration in the organic phase exceeded 0.44 mole/liter, diluent degradation was detected. Generally it may be stated that, at temperatures below 70°C, both nitric and nitrous acids must be present to form diluent degradation products.

The rate of DBP formation increased by a factor of 5 when the temperature was increased from 25 to 40°C and by 25 when the temperature was increased to 70°C. An exposure of 21 days at 40°C was required to produce a detectable amount of DBP. The rate of DBP formation at 40°C was sensitive to chemical conditions but averaged about 0.015 mole/(liter)(day) for a wide range of uranium and acid concentrations in the

organic phase.<sup>4</sup> Tests of radiation damage to pure diluents showed toluene to be more radiation-resistant than benzene and showed benzene to be more radiation-resistant than kerosene. However, when TBP was present in the diluent, the diluent radiation stability apparently followed an inverse order.<sup>5</sup>

Hanford Purex experience has shown that the over-all decontamination factor from zirconium-niobium activities is limited to a factor of  $10^4$  by the presence of degradation products.<sup>6</sup>

In the range of 25 to 400 watt-hr/liter of irradiation, the formation of DBP accounts for 65 per cent of the uranium retention in the solvent. As compared with unirradiated solvent, a radiation dose of 450 watt-hr/liter increased the uranium losses in the stripping column by a factor of 4. This radiation dosage also significantly increased the tendency toward the formation of stable emulsions.<sup>7</sup> However, DBP was removed from used solvents by scrubbing with dilute caustic, whereas other solvent degradation products were not removed by caustic scrubbing.

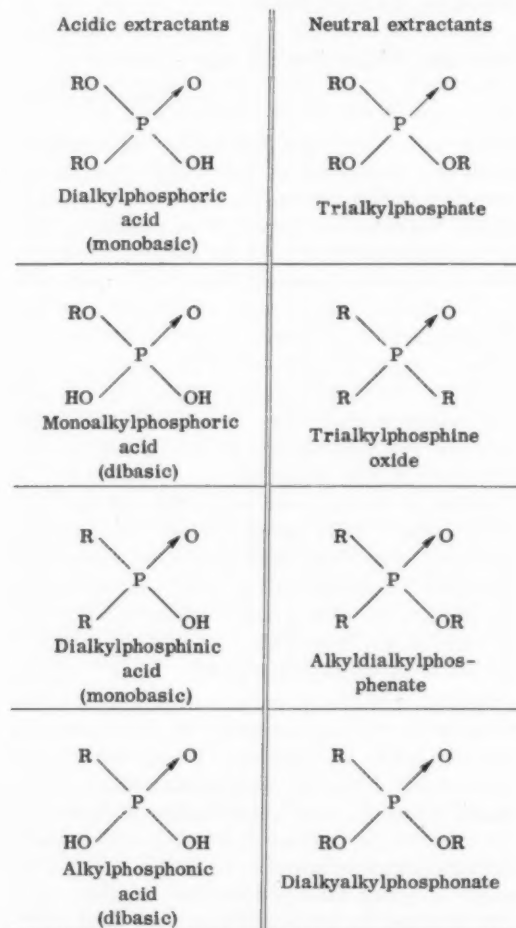
A head-end treatment with thenoyltrifluoroacetone (TTA) was demonstrated in batch tests as a means of improving zirconium-niobium decontamination.<sup>8</sup> TTA is widely employed as an extractant for analytical purposes. In general it extracts +4 ions but not +6. Better than 99 per cent of the zirconium-niobium activity was removed from Purex feed solutions by contacting it with an organic phase of TTA in benzene. The zirconium-niobium decontamination factor over two Purex cycles was improved by a factor of 100 to a value of  $2 \times 10^6$ .

#### Studies of Organophosphorus and Organonitrogen Extractants

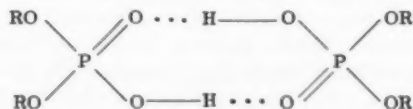
Organonitrogen and organophosphorus compounds provide a new vista of solvent-extraction schemes because they allow the application of ion-exchange principles on a solvent-extraction basis. They provide distinct advantages over ion-exchange resins in adjusting reagent concentration and selecting diluting solvent. Thus they provide greatly increased potential for selective solvent extraction. Comments presented herein on organophosphorus compounds were based on a review by Blake et al.,<sup>9</sup> and those on organonitrogen compounds were based on a review by Coleman et al.<sup>10</sup>

Useful organophosphorus compounds may be either acid or neutral. The acid reagents, in-

cluding mono and dialkyl esters of orthophosphoric acid and monoalkyl phosphoric and dialkyl phosphinic acids (see Fig. 1), allow application of cation-exchange principles on a solvent-



#### POLYMERIC (DIMERIC SHOWN) STRUCTURE OF ACID EXTRACTANTS IN MOST DILUENTS\*



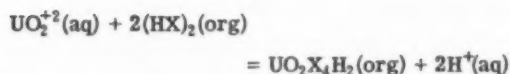
\* Polymeric structure identified by D. F. Peppard, J. R. Ferraro, and G. Mason (ANL), "Hydrogen Bonding in Organophosphoric Acids," presented at ACS meeting March 1958; to be published in *Journal of Inorganic & Nuclear Chemistry*.

Figure 1—Structure of organophosphorus extractants.



extraction basis. Extraction by the neutral reagents was similar in nature to extraction by TBP. These reagents, unlike TBP, can be used to recover uranium from nearly any solution in which it is encountered.

The acidic organophosphorus reagents extract uranium and other metals primarily by a cation exchange between the extracted metal ion and acidic hydrogen of the reagent. For example, di-2-ethylhexyl phosphoric acid extraction of uranium has the following reaction at relatively low uranium levels:



The dialkyl phosphoric acid was dimeric in the organic diluent, and the uranium extractant complex contained unreplaced acidic hydrogen. At higher uranium levels, polymers were formed.

An important property of the dialkyl phosphoric acids was that, in combination with neutral organophosphorus reagents, a strong synergistic enhancement of uranium extraction was obtained, i.e., the extraction power of the mixture was greater than the sum of the extraction powers of the separate reagents. This was probably caused by the addition of the neutral reagent to the uranyl dialkyl phosphate complex through hydrogen bonding.

The neutral alkyl phosphinates, phosphonates, and phosphine oxides may be likened to TBP in their extraction behavior as shown in the following equation:



These reagents, however, offer a greatly increased range of extraction power. Trioctylphosphine oxide, the strongest extractant, gives uranium extraction coefficients more than 100,000 times greater than does TBP from the same aqueous medium. Nitrate was the most favorable aqueous medium. An important consequence of the high extractability of nitrate solutions was that by the introduction of relatively small amounts of nitrate into much less favorable aqueous solutions, namely, sulfate and phosphate, uranium was effectively extracted by a phosphine oxide.

High molecular weight alkylammonium salts and related organonitrogen compounds extract

metals from aqueous solutions where they exist as anions or organic complexes. The versatile control of extraction by choice of amine class and structure and of diluent type makes possible the extraction of several types of metal ions from different aqueous systems and selectivity between metal ions. In general the extraction power was greatest with primary amines and decreased to secondary and tertiary amines and decreased also with increased alkyl branching and with increased polarity of the diluent. The structure of some amines of interest in solvent extraction is shown in Fig. 2.

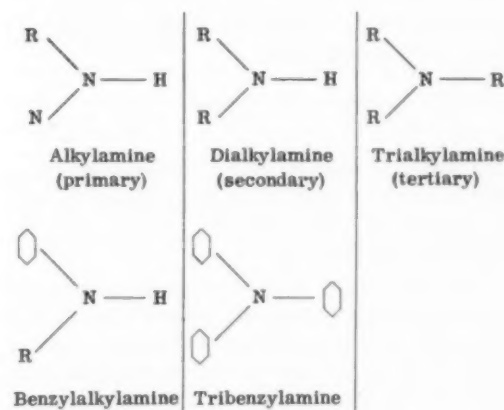
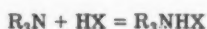


Figure 2—Structure of amine extractants.

The simple amines like weak-base resins were ineffective at high pH, whereas the strong-base quaternary ammonium compounds were effective over a wide range of pH. However, the problem of organic phase solubility was more severe with the quaternary ammonium salts than with the salts of the simple amines. The molecular or free-form base of the simple amines was soluble in many organic diluents, but the salts of some of them show limited organic solubilities, typically decreasing in the order sulfate, disulfate, chloride, and nitric. Salts of all the straight-chain primary amines showed very limited solubility in most diluents. Salts of the long straight-chain secondary and tertiary amines were sufficiently soluble, better than 0.1 mole/liter for use in aromatic hydrocarbons. Their normal sulfates were soluble in aliphatic hydrocarbons like kerosene. The bisulfates of the straight-chain secondaries separated out of kerosene solution, and those of the straight-

chain tertiaries were borderline. The solubility of the bisulfates, chlorides, and nitrates in kerosene increased on addition of alcohol and was sufficient for most process uses in kerosene modified with 3 to 5 per cent of a long-chain alcohol. When the alkyl groups were considerably branched, the salts of all three amine classes were satisfactorily soluble in plain kerosene.

Organic solutions of the amines in their free-base form extract acids from aqueous solutions to form the alkylammonium salts.



One anion was readily exchanged for another from the aqueous phase.



The order of preference in the amine solutions was similar to that in anion-exchange resins, in decreasing order chlorate, nitrate, chloride, bisulfate, and fluoride.

The versatility of the organophosphorus and organonitrogen compounds makes them readily adaptable to the separation of uranium or plutonium from fuel alloys containing aluminum, zirconium, magnesium, or stainless steel.

Tri-*n*-octylphosphine oxide was an excellent extractant for zirconium from nitrate or chloride solutions. Extraction coefficients,  $E_a^0$ , as high as 1000 were observed in 7*M*  $HNO_3$  or  $HCl$ . At lower acid concentrations, coefficients of 1000 were realized when a salting agent of aluminum nitrate or aluminum chloride was added. The extracted species was of the form  $ZrCl_4 \cdot 2TOPO$ . From sulfate or fluoride solutions, however, extraction was poor, presumably because of the formation of anionic complexes.<sup>11</sup>

Amines show promise for the separation of plutonium and uranium in high-plutonium power reactor fuels. Trilaurylamine extracts plutonium from  $HNO_3$  solutions. The extraction coefficient for plutonium decreases with uranium concentration but was considered satisfactory for plutonium recovery to uranium concentrations of 1.5 moles of uranium per liter.<sup>12</sup> In a 90 per cent xylene diluent, tri-*n*-octylamine was a better extractant than trilaurylamine, the extractant capacity being 8.9 and 4.2 g of plutonium per liter, respectively, before the separation of the amine into a third organic phase.<sup>8</sup>

The plutonium capacity of trilaurylamine was about 1 mole of plutonium per 4 moles of amine.<sup>13</sup>

Zirconium-niobium activities were difficult to strip from amines. Re-use of the organic extractant is essential to a satisfactory solvent-extraction process. Preliminary tests indicate that retained zirconium-niobium activities cannot be removed by carbonate washing, steam distillation, or filtration on silica gel. These activities can be stripped from the amine with caustic, but large volumes were required,<sup>6,12</sup> the  $E_a^0$  being about 0.7.

### Nuclear Safety, Criticality

Nuclear safety is an important consideration in the reprocessing of enriched fuels.

The possibility of exceeding criticality limits exists at very low enrichment. Aqueous solutions of uranium enriched to 0.94 per cent  $U^{235}$  cannot be made critical. However, at a slightly greater enrichment of 0.96 per cent  $U^{235}$ , a critical mass is possible where the vessel diameter is greater than 19.7 in. Ketzlach<sup>14</sup> has reported experimental data for the critical volume of aqueous solutions of low enrichment from 0.96 to 1.61 per cent  $U^{235}$ .

For fuel destined for processing by Redox flow sheets (methyl isobutyl ketone solvent), boric acid can be added to the dissolver solution as a neutron absorber. By this procedure larger batches of fuel can be processed. Boric acid creates no problem in Redox processing. In all proposed flow sheets boric acid strongly favors the aqueous phase and is eliminated in the aqueous waste stream.<sup>15</sup>

Experimental data are available on critical mass of enriched-uranium metal in the form of rods, slabs, and spheres with and without reflectors. The effect of the reflector was substantial. For Oralloy (approximately 93 per cent  $U^{235}$ ) the critical mass of the sphere was reported as 14.1 kg with a 4-in. beryllium reflector or 22.9 kg with 4 in. of water reflector. The role of the reflector was further emphasized by the critical diameter of infinite rods which was 4.9 in. in air and 2.9 in. with water reflection.<sup>16</sup> Data for Oralloy surrounded by a beryllium reflector were summarized by Ralston.<sup>17</sup> Critical mass for Oralloy spheres varied from 53 kg with no reflector to 10.765 kg with an 8-in. beryllium reflector. Wrapping the vessel with a 28-mil thickness of cadmium shielding substantially reduced the neutron interaction.<sup>18</sup>

## Precipitation Processes

Precipitation is the oldest of the separation procedures employed in fuel reprocessing. It is still found useful for certain radiochemical separations. In addition to the applications reported in this section, developments in the use of precipitation in waste disposal and homogeneous reactor fuel processing will be reported from time to time in other sections of this Review.

### Plutonium Separations Process

A historical description of the engineering development of the bismuth phosphate process for separating plutonium has recently been published.<sup>19</sup> Although the process is no longer in use, much of the experience gained in the operation of the production plant has been advantageously applied to other precipitation processes, such as scavenging processes for feed preparation and processes for removing long-lived fission products from waste streams.

The process consisted of precipitating bismuth phosphate alternately from reduced and oxidized plutonium solutions to permit a stepwise separation of plutonium, uranium, and fission products. Plutonium was concentrated by carrying on lanthanum fluoride, then isolated from the carrier by precipitation as plutonium peroxide.

A brief description of the remotely operated plant is given. Procedures for dissolution of the irradiated uranium and for treating the evolved gases are also discussed.

### Scavenging of Irradiated

#### Uranium Feed Solutions

In the preparation of feed solution<sup>20</sup> for the Purex process, the irradiated uranium is dissolved in nitric acid, and the resulting solution is sometimes scavenged with manganese dioxide. This head-end treatment has a dual purpose. It removes a substantial portion of the zirconium-niobium, iodine, and ruthenium from the feed solution, and it clarifies the feed from solids that are present after the dissolving step. As described in a previous Review (Vol. 1, No. 2), the scavenging has been accomplished by addition of potassium permanganate, followed by manganous nitrate to reduce all of the permanganate to manganese dioxide. The slurry is then heated to coagulate the precipitate, which is removed by centrifugation.

Experience showed that considerable ruthenium was evolved in this operation and was emitted as particles of submicron dimensions that were not removed by caustic scrubbers or by filters. This ruthenium "dust" was presumed to be due to reduction of the volatile ruthenium tetroxide to lower oxides. The dust was emitted in sufficient amount to constitute a hazard from the standpoint of contamination of process facilities and their immediate environment.

The production of volatile ruthenium tetroxide requires the presence of a strong oxidizing agent. Experiments were therefore conducted on a modification of the scavenging process so that the reagents would be added in reverse order (first manganous ion, then permanganate) to prevent exposure of the ruthenium to strong oxidizing agents. Results showed that manganese dioxide formed by a "reverse strike" effectively scavenged dissolver solutions without volatilizing much of the ruthenium. From 0.2 to 3.5 per cent of the ruthenium in dissolver solution was evolved during laboratory tests with the reverse strike, in contrast to 95 per cent or more for direct strike treatments.

The reverse strike head-end treatment was essentially equal to the direct strike treatment with respect to removal of most of the fission products of interest. Loss of plutonium to the manganese dioxide cake was about 0.1 per cent, essentially the same as with a direct strike.

## Ion-exchange Processes

Ion-exchange processes have been applied to (1) separation of californium, curium, and americium from each other; (2) recovery of plutonium from Purex wastes; (3) processing of PRPR fuels; and (4) removal of thorium from U<sup>233</sup>. Both anion- and cation-exchange processes have been used.

Separation factors between californium, curium, and americium on ion-exchange resin Dowex-50X-12, in ammonium form, have been calculated<sup>21</sup> from static equilibrations between pH 2 and pH 3.3 in presence of  $10^{-3}M$  EDTA. They are found to be  $2.04 \pm 0.05$  between americium and curium and  $5.5 \pm 0.1$  between curium and californium. Under the experimental conditions only 1:1 complexes are formed, and by ion-exchange techniques the dissociation constants are found to be equal to:

Californium	$10^{-19.09 \pm 0.2}$
Curium	$10^{-18.45 \pm 0.1}$
Americium	$10^{-18.16 \pm 0.1}$

Preliminary column experiments show that this complexing agent will be quite useful for separating actinide elements.

Anion-exchange processes are becoming more and more important in Purex processing.<sup>6,12,22</sup> Permutit SK, the resin currently in use in the Purex continuous anion-exchange concentration unit,<sup>12</sup> proved more stable to  $\text{Co}^{60}$  gamma radiation than other resins previously tested. At a dose of  $3.4 \times 10^8$  R this resin still possessed excellent mechanical properties and had lost only 10 per cent of its initial plutonium absorption capacity. Irradiation to  $5 \times 10^8$  R, however, destroyed completely the utility of the resin. The damage suffered in this prolonged exposure may well be due to nitrous acid-catalyzed chemical attack by the static 7M  $\text{HNO}_3$  solution which covered the resin during the irradiation. Formation of nitrous acid is known to have occurred since oxides of nitrogen were detected when the sample vial was uncapped. The absorption capacity of Permutit SK for plutonium out of a synthetic Purex waste solution containing 10 mg of plutonium per liter was determined at 25 and 60°C. The capacity proved to be virtually identical to that of Amberlite IRA-401. At 30 per cent breakthrough (corresponding to recovery of 90 per cent of the plutonium charged), the capacity was 3.24 g of plutonium per liter resin at 25°C and 1.73 g of plutonium per liter resin at 60°C. Laboratory tests disclosed no change in properties of a sample of Permutit SK removed from the Purex continuous anion-exchange unit after 16 days of operation. The capacity was determined for a sample of Permutit SK removed from a Purex continuous anion-exchange unit after 41 days of operation.<sup>6</sup> The capacity of this resin was the same as that of new resin within experimental error. A slight increase in fines was noted.

Studies of plutonium absorption and elution kinetics aimed at the screening of commercially available anion-exchange resins have been completed.<sup>12</sup> Of eleven resins tested, Dowex-1, X-4 (50 to 100 mesh) exhibited the optimum combination of absorption and elution rates. Of 20- to 50-mesh resins tested, Permutit SK proved far superior, with Amberlite IRA-401 and Dowex-1, X-4 (20 to 50 mesh) as second and third choices, respectively. Increased radiation stability

makes Permutit SK and Amberlite IRA-401 first and second choices, respectively, for processing highly radioactive feeds.

A flow sheet was tested for the separation of plutonium from uranium and fission products. Solvent extraction was carried out in miniature mixer-settler equipment. The plutonium product from the solvent-extraction equipment was fed to a fixed bed of Permutit SK resin at a column temperature of 60°C. "Complete" decontamination was obtained for all fission products except niobium. The niobium decontamination factor for the complete process from dissolver solution to plutonium product was  $4 \times 10^7$ . These results indicate the technical feasibility of replacing the Purex 1BS, 2A, and 2B columns with a single cycle of anion exchange.

The feasibility of obtaining complete fission-product decontamination of PRPR fuels by anion exchange was tested<sup>22</sup> in a two-cycle run. Feed for this run was prepared from Purex dissolver solution and contained 7.7M  $\text{HNO}_3$ , 104 g/liter U, 0.47 g/liter Pu(IV),  $1.1 \times 10^9$   $\gamma$ /(min)(ml) Zr-Nb, and  $1.6 \times 10^7$   $\gamma$ /(min)(ml) Ru-Rh. This feed was filtered twice through a glass wool filter to remove solids which filtered out on the resin column in earlier runs.

A Dowex-1, X-4 (100 to 200 mesh) column was loaded to 95 per cent capacity at 55°C and then was washed at the same temperature with 60 column volumes of 7.5M  $\text{HNO}_3$ . The wash effluent gamma activity decreased rapidly from  $7 \times 10^7$  to  $4 \times 10^5$  counts/(min)(ml) with the passage of 12 column volumes of wash solution. The wash activity decreased only a factor of 10 with the passage of an additional 48 column volumes of wash.

The plutonium was eluted from the resin at a concentration of 19 g/liter of plutonium with 0.35M  $\text{HNO}_3$  at 55°C. The gross gamma decontamination factor through this cycle was  $2.1 \times 10^4$ . Eighty-five per cent of the gamma activity in the product was due to niobium and the remainder to zirconium.

The product from this run was acidified and used as feed for a second cycle. The plutonium was loaded on a second Dowex-1, X-4 (100 to 200 mesh) column at 55°C and eluted at a concentration of 26 g/liter with 0.35M  $\text{HNO}_3$ . Gross gamma decontamination through the two cycles of anion exchange was  $3 \times 10^7$ . As measured on the gamma scintillation counter, 99.3 per cent of the gamma activity in this product was due to



plutonium and only 0.7 per cent to the fission products.

Applications of cation-exchange resins have also been found. When  $U^{233}$  is being processed,<sup>23</sup> the small quantities of  $Th^{228}$  generated by the alpha decay of  $U^{232}$ , which is present to the extent of 20 to 40 ppm, are not removed in the ordinary chemical purification. Consequently, in recycle material which is several months old, gamma activity due to the  $Th^{228}$  decay chain builds up rapidly. A process has been developed in which most of the thorium is removed by passage of 0.05M  $HNO_3$  solutions of  $U^{233}$  through cation resin.  $Th^{228}$  levels in the effluents are low enough so that the resulting solutions can be processed in unshielded dry boxes. Uranium is eluted from the resin with 10M  $HCl$ . Work is being done on recovery of thorium from this process since both  $Th^{228}$  and  $Th^{229}$  are in demand for research purposes.

### Volatility Processes

Development has continued of various aspects of volatility processing, i.e., processes in which fluorination is used to convert uranium to volatile uranium hexafluoride and decontamination is subsequently effected by distillation or by absorption techniques.

### Fused-salt Processes

One application of the fluoride volatility process is the dissolution of zirconium-uranium alloy fuels and decontamination of uranium hexafluoride. Dissolution is carried out with a hydrogen fluoride sparge, and uranium hexafluoride is removed with a fluorine sparge. Both steps utilize a molten fluoride medium at about 600°C.

In dissolution tests, mock-up fuel elements of Zircaloy-3 were completely dissolved with a hydrogen fluoride sparge while totally submerged in molten  $NaF-ZrF_4$  salt.<sup>24</sup> Dissolution rates ranged from 1 to 1.3 mg/(min)(sq cm) based on the original total area of the fuel assemblies. Hydrogen fluoride rates were 11 to 45 lb/(hr)(sq ft of dissolver cross section), and chemical utilizations were 2 to 6 per cent. Higher rates, up to 15 mg/(min)(sq cm), were observed with the zirconium above the level of the salt. A dissolution of Zircaloy-2 with hydrogen fluoride sparge was carried to completion with an average rate of 5.5 mg/(min)(sq cm) in a  $LiF-NaF$  salt.<sup>25</sup> In a 2-hr fluorination test at

600°C of an equimolar sodium fluoride-zirconium fluoride mixture containing initially 14 wt.% uranium (as  $UF_4$ ), the unrecovered uranium was only 0.014 wt.%. This initial uranium concentration<sup>25</sup> was higher than in previous tests by a factor of 2. Three fluorination runs were made<sup>26</sup> to determine the feasibility of removing uranium from a salt mixture of the composition  $LiF-BeF_2-UF_4$ . In 2.5-hr fluorinations at 550, 500, and 450°C, the uranium left in the salt was, respectively, 1, 2, and 5 per cent of the initial amount. The induction period (initial delay of  $UF_6$  release) observed with the  $NaF-ZrF_4$  salt was not found here.

### Process Chemistry of Fluoride Systems

Laboratory work has been carried out on the behavior of niobium and ruthenium fluorides in fused sodium fluoride-zirconium fluoride<sup>27</sup> using carrier-free  $Nb^{95}$  and ruthenium- $Rh^{100}$ . Niobium fluoride volatilized from the fused salt was removed effectively from a hydrogen fluoride stream by a sodium fluoride trap at 270°C. Ruthenium introduced into the fused salt as metal was not volatilized with fluorine sparge at 600°C. These results agree with results obtained earlier<sup>28</sup> with gram quantities of niobium and ruthenium fluorides.

Solubility of  $PuF_3$  in one  $NaF-LiF-BeF_2$  mixture, three  $NaF-BeF_2$  mixtures, and four  $LiF-BeF_2$  mixtures was determined<sup>29</sup> at temperatures ranging from 550 to 650°C. Solubility-composition diagrams for the binary systems at 565°C show that in the  $LiF-BeF_2$  system a minimum solubility of 0.25 mole %  $PuF_3$  occurs at about 63 mole %  $LiF$ , while in the  $NaF-BeF_2$  system the minimum solubility of 0.18 mole %  $PuF_3$  occurs at approximately 57 mole %  $NaF$ . The highest solubility observed at 565°C was 1.2 mole %  $PuF_3$  in the mixture  $NaF-LiF-BeF_2$  (56.5-17.5-26 mole %). Plutonium existed as  $PuF_3$  with no disproportionation. The compound  $NaPuF_4$  was believed found in one mixture.

The solubility of hydrogen fluoride in the system  $NaF-ZrF_4$  has also been determined.<sup>30</sup> Hydrogen fluoride has the same order of magnitude solubility and heat of solution in  $LiF-BeF_2$  as in the  $NaF-ZrF_4$  salt. Solubility studies of  $HF$  and noble gases in various fused salts are continuing.

Solubility studies of representative fission-product fluorides ( $CeF_3$ ,  $YF_3$ , and  $LaF_3$ ) in  $BeF_2$  contained in fused fluoride solvents are being made with tracer techniques. In  $NaF-BeF_2$ ,

CeF<sub>3</sub> is about one-half as soluble as in LiF-BeF<sub>2</sub> (Refs. 24 and 30). The solubility of CeF<sub>3</sub> goes through a minimum at about 63 mole % NaF. A mixture containing 53 mole % NaF dissolves about 0.1 mole % CeF<sub>3</sub> at 500°C.

The precipitation of oxides of fission products from fluoride melts is being studied as a possible method for purification of molten fluoride reactor fuel mixtures.<sup>30</sup> The following is the order of decreasing solubility observed for oxides in molten LiF-KF:

- (1) Ba, Sr, Ga, K, Na, Li
- (2) Be, Mg
- (3) Rare earths (R<sub>2</sub>O<sub>3</sub>)
- (4) U, Zr, Hf

Estimations of the magnitude of the absolute solubilities at 600°C in LiF-KF with excess precipitating agent (CaO or Na<sub>2</sub>O<sub>2</sub>) have been made as follows: zirconium, 10<sup>-3</sup> wt.%; uranium, 10<sup>-2</sup> wt.%; cerium, 10<sup>-2</sup> wt.%; beryllium, 2 × 10<sup>-2</sup> wt.%; barium, 6 wt.%.

The vapor pressure of CsF-BeF<sub>2</sub> from 800 to 1050°C has been measured.<sup>24</sup> At 950°C, pure CsF has a vapor pressure of 43 mm Hg, and pure BeF<sub>2</sub> has a vapor pressure of 33.5 mm Hg. At this temperature a mixture containing 30 mole % BeF<sub>2</sub> has a total vapor pressure of 11 mm Hg, and a 80 mole % mixture has a total vapor pressure of 33 mm Hg. Between 80 and 100 per cent BeF<sub>2</sub>, the total pressure is independent of composition.

### Pyrometallurgical Processing

Experimental investigations on pyrometallurgical processes are in progress at several sites. These processes offer promise of reduced processing costs through elimination of chemical conversions and the ability to process short-cooled fuels. Development of pyrometallurgical processes is being carried out principally at (1) Argonne National Laboratory (ANL) on the melt refining process for the EBR-II reactor and on zinc recrystallization processes; (2) at Atomics International on the Pyrometallurgical Refabrication Experiment; (3) at Los Alamos on the processing of plutonium-rich fuels; (4) at Ames on fuel alloys, container materials, and general process investigations; and (5) at Brookhaven on Liquid Metal Fueled Reactor (LMFR) fuel processing (described under Homogeneous

Reactor Processing, p. 19). Smaller scale efforts are being made by Hanford in connection with the Plutonium Recycle Program (PRP), by ORNL on the Hermex or mercury crystallization process, and by Nuclear Metals, Inc., on crystallization processes.

### Melt Refining Studies

The melt refining process for EBR-II fuel consists simply in melting the fuel in a zirconia crucible and holding it molten for several hours at an elevated temperature (1300 to 1400°C). Considerable fission-product removal is realized through volatilization and drossing reactions. Recent work has been devoted to the removal of zirconium.<sup>31</sup> This element is not removed by oxide drossing, and there are indications that its presence in the high concentrations which would result in recycled EBR-II fuel is deleterious to the radiation stability of the fuel. The most promising method of removal is through carbide drossing effected by melting in a graphite-coated zirconia crucible. Adequate removal of zirconia (~50 per cent) with purified ingot yields of 90 to 95 per cent have been demonstrated on a 5-kg scale. Removal of cerium by preferential oxide formation does not seem to have been impaired. The effect of the graphite on plutonium recovery from high-concentration plutonium alloys remains to be investigated.

Recent work with material containing fairly high concentrations of rare gases (NRX-irradiated material, Chalk River, Ontario at about 0.15 per cent burn-up) showed essentially quantitative evolution of rare gases, confirming previous suspicions that the dross retains a large fraction of these gases when present in very small concentrations. Retention of iodine (0.24 per cent) was also smaller than found in previous work at low levels. Further experiments are being carried out on iodine behavior.

The processing of sodium-coated EBR-II pins on a 2-kg scale has resulted in lower ingot yields (around 90 per cent) because of the presence of an oxide skin on the surfaces of the pins.

Work continues on the design of the process building and equipment for processing EBR-II fuel at Arco, Idaho. The Stewart Construction Company of Tucson, Arizona was awarded the contract for the construction of the Laboratory and Service Building.

### Separation of Fissionable and Fertile Materials

Pyrometallurgical processes are being developed for the recovery of fissionable materials ( $\text{Pu}^{239}$  or  $\text{U}^{233}$ ) bred in uranium or thorium blankets. Previous Reviews in this series have described the removal of plutonium from uranium by extraction into magnesium or silver, both of which are essentially immiscible with a molten uranium phase. Another system of considerable interest which has been described previously is the magnesium-thorium system in which uranium has a very low solubility.

A new procedure which has promise for uranium-plutonium separation is based on the low and high solubility, respectively, of uranium and plutonium in a 46 wt.% magnesium-zinc eutectic.<sup>31</sup> After dissolution in zinc, both may be precipitated by cooling, and, after separation from the zinc mother liquor, separation of the two can be effected by addition of the appropriate amount of magnesium to form the eutectic. From the available data it appears that plutonium can be concentrated with high yield from 1 up to about 40 wt.% in uranium by this procedure.

Use of ultrasonic energy is being investigated as a means of mixing the immiscible magnesium and uranium-5 wt.% chromium phases of the magnesium extraction process mentioned above.<sup>32</sup> A tantalum vibrator,  $\frac{3}{4}$  in. in diameter, has been employed in the uranium-chromium system and in the two-phase system at 900°C. No indication of attack was apparent in either case after 2 hr of operation at a frequency of 20 kc and an energy input of 200 watts.

### Processing of Plutonium-rich Fuels

In previous Reviews, studies carried out at Los Alamos have been reported on processing plutonium-rich fuels by oxide slagging and liquation. The plutonium alloy employed is generally a synthetic plutonium-iron alloy containing fission-product elements in expected process concentrations. The status of work on process investigations was recently reported.<sup>23</sup> Oxide slagging and liquation both show promise for fission-product separation. Carbide slagging was effective in reducing the concentration of zirconium, a major fission-product element, but, because of a simultaneous high loss of plutonium, it appears unattractive. Halide slagging results in conversion of plutonium to the chloride and would necessitate subsequent reduction back to metal. However, considerable fission-product

removal may be realized by the metal-to-salt-to-metal phase transfers of plutonium.

Excellent purification from zirconium, molybdenum, ruthenium, lanthanum, and cerium has been achieved by electrorefining using a molten salt bath composed of lithium, potassium, and plutonium chlorides in the respective relative weight amounts of 41, 50, and 9. An iron cathode was employed to permit collection of the product as a molten plutonium-iron alloy.

Work also has continued on the development of a mercury precipitation process. Plutonium solubility increased from 2.65 g/ton at 20°C to 85.7 g/ton at 325°C. From individual fission-product solubility measurements, it was concluded that good purification is possible provided solid and liquid phases can be well separated, which has been a difficult problem.

Molten metal extraction using a 68 wt.% calcium-magnesium eutectic which has limited solubility for plutonium resulted in poor extraction of plutonium, iron, ruthenium, molybdenum, niobium, and zirconium and good extraction of lanthanum and cerium.

### Uranium Oxide Fuel Processing

Work has continued on chemical pulverization of  $\text{UO}_2$ -fission pellets (0.8 wt.% fission-product oxides as stable isotopes).<sup>33</sup> Successive treatments with air (3 hr at 375°C) and hydrogen (3 hr at 650°C) reduced the particle size to 95 per cent less than 400 mesh. Large-scale equipment for chemical pulverization is now being built. Extraction of fission products from  $\text{UO}_2$  by treatment with HCl gas appears promising.

As part of the PRP efforts are being made to develop efficient chemical processing methods and equipment for preparation of plutonium fuel alloys or oxide elements, for recovery of plutonium from irradiated fuel elements, and for restoring the plutonium content of depleted uranium.<sup>34</sup> Pyrochemical methods are being sought for increasing plutonium content of depleted plutonium-uranium alloy fuels which, in general, involve reduction of plutonium or uranium oxides. Methods under investigation for fuel-alloy preparation include aluminum-cryolite reduction of plutonium dioxide to form plutonium-aluminum alloys, and removal of aluminum by oxidation and slagging into cryolite, by volatilization as  $\text{AlF}$  or as  $\text{AlCl}_3$ , and by precipitation of  $\text{PuAl}_4$  (concentration method). Oxidation of aluminum and drossing into cryolite resulted in

the cryolite layer becoming heavily laden with  $\text{Al}_2\text{O}_3$  producing a cement-like mass. The other three methods are promising.

In connection with the processing of oxide fuels,  $\text{UO}_2$  may be reduced aluminothermically at around  $725^\circ\text{C}$  in the presence of  $\text{KAlCl}_4$  (Ref. 35). The extent of reduction is between 90 to 100 per cent. In the two-phase system, aluminum and  $\text{KAlCl}_4$ , uranium would therefore be found in the metal phase. Plutonium, however, distributes almost quantitatively into the salt phase. An examination of the literature on free energy changes for solution of salts in a  $\text{KCl-LiCl}$  eutectic shows the greatest negative change for solution of  $\text{AlCl}_3$ . This is evidence that solution of  $\text{AlCl}_3$  provides driving force for reduction of uranium oxide by aluminum.

A method of processing oxide fuels based on the above would involve reduction of both plutonium and uranium oxides in aluminum and molten cryolite, separation of phases, and contacting the metal phase with  $\text{KAlCl}_4$  to extract the plutonium. It is believed that plutonium may be recovered from the salt phase by calcium or magnesium reduction. Preliminary fission-product data show good removal of cesium, barium, and strontium into the cryolite layer. Subsequently, the rare earths accompany the plutonium into the salt phase, while ruthenium and zirconium remain largely in the metal phase.

#### Fractional Crystallization Processes

Several processes are under investigation which involve dissolution of the fuel or fertile metal in a metal solvent, precipitation as an intermetallic compound with the solvent by cooling, and, after separation of the intermetallic compound, recovery of the desired metal by vaporization of the solvent metal. In the Hermex process, mercury is the solvent metal; in the Pyrozinc process, zinc is the solvent. Recently cadmium has been examined as a solvent for uranium because of potential advantages with respect to materials of construction. (The solubility of uranium in cadmium was measured at temperatures up to  $475^\circ\text{C}$ , where its solubility was 2.25 wt.%. Phase transitions occur above this temperature.) Recent work on these processes has included solubility measurements, examination of fission-product behaviors, and fundamental studies of the systems.

Molten zinc at  $700^\circ\text{C}$  dissolved rotating uranium rods so rapidly that meaningful dissolution

rate measurements could not be taken. Rates are now being obtained at  $500^\circ\text{C}$ . The solution rate does not appear to be noticeably affected by saturation or unsaturation of the melt with uranium.<sup>31</sup>

The use of protective chloride fluxes to permit operation in air has been considered. Small concentrations of magnesium in the metal phase ( $\sim 0.5$  wt.%) have been used to prevent oxidation of the uranium. It was demonstrated<sup>31</sup> that oxidation of the uranium did not commence until the magnesium content had been reduced to below 0.08 wt.%. Preliminary examination of distribution of fission products into the salt layer showed transfer of cerium, cesium, strontium, and tellurium and retention of uranium, plutonium, zirconium, and niobium. Attainment of equilibrium appears to have been still incomplete after 6 hr of agitation.

The measured free energy of formation of  $\text{U}_2\text{Zn}_{17}$  in equilibrium with saturated zinc solution has been determined to be<sup>31</sup>

$$\Delta F = -53,717 + 38.242 T$$

Considerable work has been carried out on the thorium-zinc and zirconium-zinc phase diagrams.<sup>36</sup> In addition to  $\text{Th}_2\text{Zn}_{17}$ , three other compounds have been identified in the thorium-zinc system:  $\text{ThZn}_4$ ,  $\text{ThZn}_2$ , and  $\text{Th}_2\text{Zn}$ .

Uranium solubility in mercury was measured and was found to increase from 0.0048 to 1.1 wt.% as the temperature was increased<sup>37</sup> from 25 to  $356^\circ\text{C}$ . Over the same temperature range the ruthenium solubility increased from  $0.9 \times 10^{-7}$  to  $3.5 \times 10^{-7}$  wt.%, indicating high potential separation of ruthenium and uranium if suitable separation efficiency could be realized. In the 0.1 wt.%  $\text{Mg-Hg}$  system, the uranium solubility was 1.4 wt.% at  $356^\circ\text{C}$ .

Fractional precipitation processes for bismuth-based liquid metal fuel systems were recently discussed by Teitel.<sup>38</sup> Two systems, a solution of uranium in bismuth and a dispersion of  $\text{USn}_3$  in a low melting lead-bismuth-tin alloy, were investigated. Data are presented for the distribution of fissile and fission-product elements between solid and liquid phases.

#### Miscellaneous Pyrometallurgical Studies

All efforts to increase the reduction yield of  $\text{UF}_6$  by sodium amalgam to above 40 per cent have been unsuccessful.<sup>37</sup> With a lithium amal-



gam, 84 per cent reduction was achieved at 25°C. Excess lithium was required for high yields.

Roland<sup>39</sup> reports equilibrium constants and free energy for oxidation reactions occurring in molten uranium. Deoxidation reactions of interest were those possible by use of aluminum, beryllium, carbon, calcium, magnesium, and zirconium.

Wisnyi and Pijanowski<sup>40</sup> reported the melting point of  $\text{UO}_2$  as  $2760 \pm 30^\circ\text{C}$  and established the cubic form as the stable phase.

Ackerman and Thorn<sup>41</sup> have reported thermodynamic data of gaseous  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}$ ,  $\text{ThO}$ ,  $\text{ZrO}_2$ ,  $\text{ThO}_2$ ,  $\text{TaU}_2$ ,  $\text{UO}_2$ , and  $\text{WO}_3$  in equilibrium with solids at temperatures above  $1700^\circ\text{C}$ .

Cerium solubility in uranium was reported<sup>33</sup> to be 0.7, 1.8, and 2.2 wt. % at 1140, 1200, and  $1345^\circ\text{C}$ .

Some basic chemistry studies including measurements of the vapor pressure of thorium and thorium tetrafluoride, studies of the  $\text{Bi-BiCl}_3$ ,  $\text{Cd-CdCl}_2$ , and  $\text{Cd-CdI}_2$  systems, and vaporization studies carried out on  $\text{La}_2\text{O}_3$ ,  $\text{BeO}$ ,  $\text{ZrC}$ , and  $\text{Be}_2\text{C}$  were recently reported.<sup>42</sup>

## Homogeneous Reactor Processing

### Aqueous Homogeneous Reactors

It was reported in the previous Review<sup>43</sup> that the chemical processing plant installed as an integral part of the Homogeneous Reactor Test (HRT) was preparing to make active runs. This was to be done in conjunction with operation of the reactor. During the past period a leak developed between the core and blanket systems in the reactor proper. Efforts to locate the leak and determine its nature have been unsuccessful to date, but on the basis of tests it was concluded that no modifications were necessary for reactor operation to continue. The rate of intermixing between core and blanket<sup>24,26</sup> was substantially constant at 3 to 4 lb/min.

Iodine adsorption by silvered stainless-steel York-mesh continued to be studied. It was established that the removal rate from an oxygen-steam-iodine mixture was eight times faster at  $150^\circ\text{C}$  than at  $110^\circ\text{C}$ . Corrosion measurements of the silvered York-mesh by uranyl sulfate at 100 and  $110^\circ\text{C}$  were made. The composition was 10 or 40 g of uranium per kilogram of water with 50 mole % excess sulfuric acid. Attack at

$100^\circ\text{C}$  was negligible. However, at  $110^\circ\text{C}$  the attack was sufficiently severe so that the silver was loosened from the supporting surface after 24 to 48 hr. No such behavior was observed in any gas phase test containing oxygen and steam at  $120^\circ\text{C}$  after several hundred hours. In further tests it was established that in a steam-oxygen mixture (10 per cent  $\text{O}_2$ ) at  $150^\circ\text{C}$ , and with 60 per cent of the silver in the York-mesh packing reacted, oxidation and subsequent destruction of the packing occurred. Silvered York-mesh containing no iodine was subjected to comparable environments and was not affected. General conclusions in the iodine study to date are that Columbia grade G activated charcoal is a superior adsorbent. Linde molecular sieve materials are 20 to 40 per cent as effective as charcoal, whereas silica gels are 10 to 15 per cent as effective.<sup>28</sup> The effect of diluent gas was studied on Columbia G charcoal. Adsorption was most efficient when helium was the diluent gas and was lower by a factor of 3 when helium was replaced by oxygen, hydrogen, argon, or air. A topical report on a proposed method for removal of radiiodine vapor appeared during the period.<sup>44</sup>

The adsorption of plutonium on the walls of stainless-steel loops continues to be a problem in the anticipated processing schemes for the uranyl sulfate blanket. Plutonium was injected as the sulfate into circulating fuel at  $250^\circ\text{C}$  under an oxygen pressure of 350 to 400 psi at the rate of 1 g every 8 hr. More than 95 per cent of the plutonium adsorbed on the walls of the loop. The adsorption was as much as  $2.2 \text{ mg/cm}^2$ . The corrosion scale and adsorbed plutonium were completely removed by three successive passes of  $0.4 \text{ M CrSO}_4$  and  $0.7 \text{ M H}_2\text{SO}_4$ .

An effort was made to determine whether nickel could be removed from the HRT fuel by electrolysis in a simple cell. Little success has been achieved to date. Conditions were sought under which nickel could be removed electrolytically from solutions simulating those expected in the outer dump tanks of the HRT.<sup>26</sup>

### Liquid Metal Fueled Reactors

The Liquid Metal Fuel Reactor Experiment (LMFRE), under the direction of Babcock & Wilcox Co., involves processing of radioactive gases and fission products carried in the liquid bismuth-base fuel. A new concept of containment and recirculation of volatile fission products at

the reactor has been adopted in place of charcoal adsorption. The cooled gases furnish an inert atmosphere, and necessary processing can be done on much cooler material. A gas sparger is being developed to remove volatile fission products from the liquid fuel.

Development of a fused-chloride extraction process for LMFR fuel continues.<sup>46</sup> An improved method of drying  $MgCl_2$  before making up the  $NaCl$ - $KCl$ - $MgCl_2$  eutectic results in a more reproducible uranium partition coefficient in salt-bismuth equilibrations. The same coefficient is obtained whether the uranium is originally in the bismuth or in the form of  $UCl_3$  in the salt. There is still a tendency, however, for the coefficient to level off at the higher magnesium concentrations.

At Horizons, Inc., under a BNL research subcontract, solutions of  $BiCl_3$  in  $NaCl$ - $KCl$ - $MgCl_2$  and of magnesium, zirconium, and uranium in bismuth have been successfully prepared by the electrochemical cell technique. Problems with low current efficiencies have been encountered.<sup>46</sup>

At the American Smelting and Refining Company, under another BNL subcontract, it has been found that the addition of about 0.5 per cent zinc to bismuth, followed by cooling close to the freezing point, is sufficient to remove almost all the ruthenium, rhodium, palladium, and tellurium; original concentrations of up to about 100 ppm are reduced to about 1 ppm. It appears that intermetallic sludging with zinc will be the basis of a very satisfactory process for the removal of the noble fission products from LMFR fuels.<sup>45</sup>

Salt-metal distribution coefficients for several important elements have been compiled from numerous experiments and have been plotted as a function of magnesium concentration in the bismuth phase.<sup>47</sup> The important FPS class of fission products have salt extraction coefficients about 50 times higher than uranium. These are plotted in Fig. 3. In similar tests tracer levels of  $Po^{210}$  showed that in salt-bismuth equilibrations 98 to 99 per cent of the polonium remained in the bismuth phase.

Tests were made of chloride content of bismuth. Both before and after equilibration with ternary salt at 500°C, the bismuth contains less than 2 ppm chloride, the limit of detectability.

Further runs on extraction from bismuth drops in fused-chloride salt confirm that 2-mm size droplets falling 1 ft in 2.6 sec at 500°C have their samarium contents reduced from

200 to 50 ppm. These rates are faster than expected from molecular diffusion within the drop.

The activity coefficient of zirconium in very dilute bismuth solutions was found to be  $7 \times 10^{-4}$  at 700°C (Ref. 45); that for uranium in dilute bismuth solution was  $1 \times 10^{-5}$  at 500°C (Ref. 48).

In polonium equilibration experiments, it was found that >99 per cent of the polonium remained in the bismuth. The effects of adding magnesium to the bismuth,  $BiCl_3$  to the salt, and air to the systems were insignificant.<sup>49</sup> The solubilities of 13 fission products in bismuth have been reported.

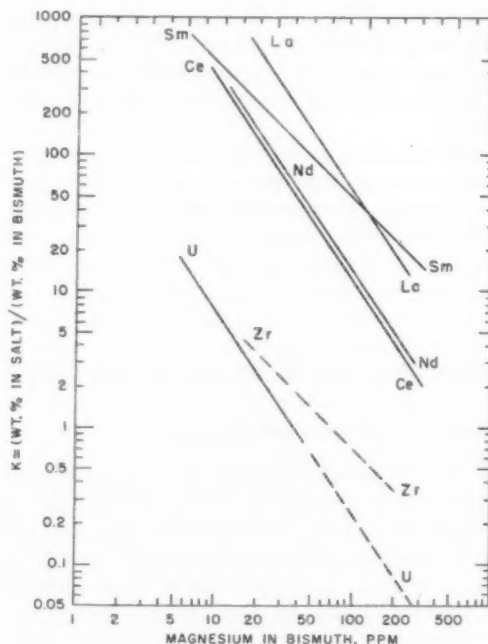


Figure 3—Distribution of solutes between  $MgCl_2$ - $NaCl$ - $KCl$  and bismuth-magnesium.

The adsorption of fission products and solutes from bismuth on graphite was examined.<sup>50</sup> Graphite disks were exposed to bismuth containing magnesium, zirconium, and a samarium tracer. Only 0.2 per cent of the samarium transferred to the graphite in the longest exposure (15 min). Xenon and iodine penetration in graphite capsule tests made thus far show that both iodine and xenon are found in essentially uniform concentrations throughout the graphite, which consisted of three successive layers each 1.5 mm thick. The diffusion of both

iodine and xenon is sufficiently great to equalize all concentrations in less than 75 hr.

## Corrosion

Problems associated with corrosion are an integral part of each process development program. Since the problems are usually unique, it becomes necessary to set up specific corrosion programs and since much of the literature is reported under this heading, this section will attempt to cover the subject for all the areas of interest.

### Solvent-extraction Processes

A number of head-end treatments are being considered for existing solvent-extraction facilities to allow the processing of fuels that cannot be directly accommodated in present plants. Efforts are being made to determine the feasibility of a single dissolver philosophy for the processing of a number of anticipated power reactor fuels. One such study proposes the use of Hastelloy F as a material of construction for a single dissolver to process zirconium, stainless steel, and aluminum matrix fuels.<sup>12</sup> In this proposal zirconium would be dissolved by the Zirflex process (see p. 6), stainless steel by  $\text{HNO}_3$ -HF mixtures, and aluminum by  $\text{NaOH}$ - $\text{NaNO}_3$  mixtures. The proposal is based on the results of corrosion tests conducted with these environments on Hastelloy F. Other processing combinations consistent with a single vessel dissolver philosophy are considered possible.

A continuing study of the corrosion of Hastelloy F to simulated Zirflex dissolver solutions is being made. At 125°C the observed corrosion rate was 0.6 mil/month, and no localized effects were noted.

Further evaluations of Hastelloy F (and other metals) in  $\text{HNO}_3$ -HF mixtures are being made. The most significant observation made to date is the high sensitivity of weld metal to localized attack. In exposures to 1M  $\text{HNO}_3$ -2M HF (temperature not given), the weld metal was found to corrode at a rate 10 times that of the base metal. This difference was much less evident in the absence of hydrofluoric acid. A solution heat-treatment at 2150°F followed by water quenching seems to eliminate the localized effect.

Other metals recently tested in boiling 1M  $\text{HNO}_3$ -2M HF are gold and platinum.<sup>8</sup> The re-

sistance of both materials is good. However, Hastelloy F was found to be severely attacked by Zirflex solution when coupled galvanically to the gold.

As reported in the preceeding Review<sup>43</sup> it is proposed to dissolve thorium and thoria-bearing fuels (after decladding) in 13M  $\text{HNO}_3$ -0.5M HF. At the end of this dissolution, the final Thorex solution would be 8.5M  $\text{HNO}_3$ , 0.05M  $\text{F}^-$ , 1M thorium nitrate. The stainless-steel cladding would be removed with boiling 6M  $\text{H}_2\text{SO}_4$ . Continuing tests with Carpenter 20 Cb are being made.<sup>7,51</sup> Recent emphasis has been placed on two types of cyclic testing: (1) 3 hr in 6M  $\text{H}_2\text{SO}_4$  followed by 5 hr in final Thorex solution containing 0.2M aluminum and (2) 3 hr in boiling 4M  $\text{H}_2\text{SO}_4$  and 5 hr of initial Thorex solution plus 0.2M aluminum. In study (1) the corrosion rate was decreased from 3 to 2 mils per month, whereas in study (2) the rate has decreased from 5 to 2 mils per month as the exposure time increases. In each case the cycled rates were 5 to 25 per cent greater than the sum of the rates measured on the individual environments.

The corrosion of stabilized Carpenter 20 Cb was previously reported as 50 to 100 mils per month in the initial Thorex dissolver solution. In recent tests in boiling final solution, the rate was 0.7 mil per month, a considerable reduction over that in the initial solution.<sup>52</sup> The decrease is thought to be due to the complexing of the fluoride ion by the thorium present in the solution.

Titanium is being subjected to boiling 8M  $\text{HNO}_3$  contaminated with trace quantities of hydrofluoric acid.<sup>53</sup> In the range of 0 to 200 ppm fluoride ion, a linear relation was observed between the fluoride content and the logarithm of the corrosion rate. The latter varied from 2 mils per month at 0 ppm fluoride to 300 mils per month at 200 ppm fluoride.

### Fused-salt Volatility Process

In this process zirconium matrix fuels are first dissolved by hydrofluorinating them in a molten fused-fluoride environment. Dissolved  $\text{UF}_4$  is converted to  $\text{UF}_6$  in a second step in which fluorine or some other strong fluorinating agent is passed through the molten melt. Graphite was previously reported to be promising in the dissolution environment. Testing of nickel-

molybdenum alloys, INOR-1,\* and INOR-8\* has continued.<sup>54</sup> These alloys continue to show average corrosion of less than 2 mils per month in equimolar sodium fluoride-zirconium fluoride in the presence of flowing HF at 650°C. Some impingement effects due to flowing HF have been observed but not evaluated. An alternate melt of molten lithium fluoride-sodium fluoride is being considered for the testing.

In some process designs the use of graphite would require a backup metal. Under such conditions the carburization resistance of the metal becomes of interest. A study of the compatibility of a number of metals with graphite was recently made and reported.<sup>55</sup> These studies were made in 250-hr tests at 1850°F and in 1000-hr tests at 1650 and 1850°F. The test metal was held in intimate contact with the graphite, and the extent of reaction was based on metallographic examination and hardness traverses. Several conclusions were made. Inconel X and "L" nickel appear to be promising materials for use in contact with graphite up to 1850°F. "L" nickel, although less resistant than Inconel, is superior to Nichrome 5, Inconel, 316 stainless steel, and 318 stainless steel. Copper, chromium, and, to a lesser extent, nickel are effective as barriers for the diffusion of carbon into stainless steel.

The fused-chloride salt extraction process for bismuth fuels uses a ternary eutectic of sodium chloride, potassium chloride, and magnesium chloride to which an oxidant, bismuth chloride, is added. Molybdenum and tantalum were simultaneously exposed to a bismuth and a salt phase in a rocking furnace test.<sup>48</sup> The bismuth phase contained 1000 ppm uranium, 350 ppm magnesium, and 350 ppm zirconium. The salt phase was the ternary eutectic. The test ran for 1000 hr with cold and hot end temperatures of 450 and 500°C, respectively. The molybdenum specimen lost no weight nor suffered any measurable depth of penetration. The tantalum weight loss was 0.1 to 0.43 per cent, and the maximum penetration was 0.6 mil. Similar tests were made in the eutectic salt phase only with 304L, 310, 316, 347, 410, and 446 stainless steels, Inconel, and molybdenum.<sup>49,50</sup> The greatest intergranular attack in the stainless steels (3 mils)

was observed in the 347. The Inconel was attacked to a depth of 0.3 mil; the molybdenum suffered no intergranular penetration at all. On the basis of the latter tests, none of them can be eliminated from consideration.

### Pyrometallurgical Processing

Tests are continuing to find a satisfactory material of construction for use with molten uranium and uranium alloys. Current efforts indicate that yttrium may be useful. Three runs in which yttrium was exposed to molten uranium-chromium eutectic have been completed.<sup>56</sup> These were as follows: (1) a static test, 550 hr at 900°C; (2) a static test, 1000 hr at 900°C; and (3) a rocker test, 1000 hr at 925°C. Micrographic examination revealed no attack at the interface in any of the tests. Yttrium oxidizes severely at elevated temperatures and requires some protection. Type 446 stainless steel is presently being used. In another test a molten eutectic of aluminum-thorium-uranium was exposed to yttrium for 1100 hr at 700°C. The walls were wetted, but the corrosion observed was small. The same eutectic caused the failure of tantalum in 96 hr at 1000°C.

Corrosion studies involving the containment of molten plutonium are of interest for pyrometallurgical processing. In experiments in which tantalum was tested as a potential material of construction, it appeared that the oxygen content of the plutonium promoted mass transfer of tantalum. In the presence of strong oxygen getters such as calcium, the mass-transfer effect was immediately reduced. Most of this work<sup>23,57</sup> was conducted at 700°C.

### Waste Calcination

One of the methods being investigated to reduce the volume of storage wastes at the chemical processing plants is the calcination of such wastes in fluidized beds. Corrosion tests for this application are presently being made. Present planned operations of such beds use temperatures on the order of 400°C. In general the austenitic stainless steels appear to be satisfactory construction materials in this service.<sup>58</sup> Stainless steel type 347, Carpenter 20, and carbon steel were recently exposed in one of the fluidized beds. Exposure time was 436 hr at 400°C. All alloys suffered minor corrosion damage. Following this exposure, the same

\*Experimental nickel-molybdenum alloys with following compositions (wt.%): INOR-1, 15 to 20 Mo, 0.5 Al, balance Ni; INOR-8, 10 to 20 Mo, 5 to 10 Cr, 4 to 10 Fe, balance Ni.



coupons were placed in the gas stream above the fluidized bed for an additional 242 hr. Maximum total attack observed was 0.41 mil per month on the 347 stainless steel.

Titanium was recently substituted into the atomizing feed jet because of an earlier failure of type 304 stainless steel in this service. The material being sprayed with the jet was 2.2M aluminum nitrate, 0.008M mercuric nitrate, 0.15M sodium nitrate, and 1.33M acid. The throat of the feed nozzle suffered complete intergranular attack after about 900 hr of service.

#### Miscellaneous Aqueous Corrosion

Two topical reports appeared during the quarter that are of general interest for processing applications. The first treats the corrosion of monel and 70-30 cupro-nickel in aqueous hydrofluoric acid.<sup>59</sup> Monel was found to be satisfactory for acid concentrations of 10 to 70 per cent at 140°F and for 38 to 48 per cent acid at the boiling point. Cupro-nickel is useful in part of these ranges. Elimination of oxygen is essential in this environment in order to achieve maximum corrosion resistance. In the absence of oxygen no accelerated interface attack was noted in the monel but some was observed in the 70-30 cupro-nickel. The use of silver solder as a joining technique should be avoided where possible. The galvanic couples created could lead to excessive corrosion of the nickel alloy.

The second report, although directed primarily toward uranium ore processing, is applicable as well to fuel processing.<sup>60</sup> The study involved the exposure of type 347 stainless steel to boiling digest liquors. This is the solution resulting from the digestion of uranium ore concentrates in a nitric acid solution. Typical concentration in grams per liter of such a liquor is as follows: Uranium 157, free nitric acid 23, total nitrate 210, sulfate 36, fluoride 0.2, and chloride 0.1. Corrosion studies on typical liquors indicate that they should not be excessively corrosive to type 347 stainless steel. Higher fluoride levels are anticipated in the future, and corrosion tests show an increasing rate of attack with increasing fluoride and also show how the latter can be controlled by aluminum additions. The tests also indicated that 304L stainless steel and Carpenter 20 appear to be comparable in resistance to type 347 stainless steel.

## Instrumentation and Equipment Development

A method for determining the plutonium concentration in any portion of a process by means of the neutrons from spontaneous fission or from alpha-neutron reactions has been developed. Aqueous solutions in the concentration range from 0.1 to 100 g/liter can be analyzed with a precision as good as  $\pm 5$  per cent.

In-line instruments require reproducible, air-free samples. Consequently, when instruments are used in conjunction with a jet airlift sampler, some means must be provided to obtain a flow of air-free liquid to the instruments. A degasser that was developed to provide a stream containing more than 99.9 per cent liquid (by volume) from a circulating mixture containing as much as 95 per cent air has been described.<sup>61</sup> This separation held for flow rates up to 500 cc/min and for air-to-liquid volume ratios up to 20:1.

A pump suitable for pumping thorium oxide slurries has been developed.<sup>62</sup> Two pumps have been built and run with an accumulated out-of-pile operating time of about 200 hr at 200 to 250°C. Flow rate was approximately 1 liter/min against a 10-ft head.

A liquid-level transmitter developed for HRT has operated for approximately 8000 hr in the mock-up. This transmitter consists of a 5-in. long float displacer supported by two helical springs. The only nonwelded closure is the 2500-psi ring-joint flange, which makes the unit amenable to remote replacement. The transmitter is also self-draining. The shift of signal level was found to be linear and amounted to about 1 per cent per 500 psi change in pressure.

The HRT outer-storage tank liquid-level transmitter has been described. It has a range of 0 to 47 in. of water and a design pressure rating of 500 psi. It is also designed for remote adjustment or replacement. Three types of linear differential transformers suitable for sensing the displacer or float motion in the above transmitters are described. The units are made radiation-resistant by eliminating all organic materials, and the design is suitable for operation at elevated temperatures.

Seven prototype models of pressure transmitters, designed to operate in a temperature range from ambient to 1400°F and measure

corrosive fluids from 0 to 200 psig, were tested to evaluate the units in operating environments. Six units of each type were tested.

A type of probe is described which allows continual indication of liquid level in a liquid metal system with liquid-level ranges from 2½ to 30 in. It operates on the principle that the liquid metal surrounding a thin-wall Inconel pipe has a much lower resistance than the Inconel pipe itself. Three-volt 60-cycle power at approximately 20 amp is used, the output being 0 to 40 mv, 60 cycles. A vacuum-tube voltmeter can be used to measure the output voltage. The units are accurate to about 1 per cent for a 7-in. probe, with a zero shift of 3 per cent from room temperature to 1400°F. Primary difficulty is in initial wetting of the Inconel probe.

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### Operating Experience

There has been reported results of extensive sampling of air and soil in the vicinity of Los Alamos to determine the degree of hazard which exists from the emission of approximately 13 grams of plutonium over a period of nine years.<sup>1</sup> It was concluded that this rate of emission did not result in contamination of the soil to an extent which would cause a health hazard since the resulting soil concentrations found are lower than the level of concern by approximately a factor of  $10^4$ . It was also determined that an emission rate of approximately  $10^6$  disintegrations of plutonium per minute under conditions prevailing at Los Alamos could not create average air concentrations in excess of permissible values.

Since 1952 the British establishment at Windscale in Cumberland on the Irish Sea has been discharging activity into the sea through a pipeline which extends approximately 3 kilometers beyond the high water mark.<sup>2</sup> An intensive program to monitor the effects of discharging wastes thusly has been carried out by the British, and the results obtained through 1956 have now been published.

The mean rate of activity discharge is reported to be 2500 curies per month over five years. This rate has been increasing. The values for the year 1956 are given in Table V-1.

Table V-1 DISCHARGE OF LIQUID RADIOACTIVE WASTE TO THE SEA FROM WINDSCALE WORKS<sup>3</sup>

Isotope	Mean discharge rate (curies per month)
Total beta activity	6100
Sr <sup>90</sup>	106
Sr <sup>90</sup>	150
Ru <sup>103</sup>	120
Ru <sup>106</sup>	2700
Pu <sup>239</sup>	3.8

The results of preliminary hydrographic and biological studies, followed by extensive monitoring of the marine environment over five

years of discharge of radioactivity, have shown the following general pattern of dispersal of activity in the sea off Cumberland. The discharged effluent is rapidly diluted with large volumes of sea water and is carried to and fro along the coast over a distance of a few kilometers by the oscillating tidal stream. Beyond the range of this movement, the activity is removed by the process of eddy diffusion, and the concentration falls to negligible levels in a few tens of kilometers. Much of the radioactivity becomes absorbed onto fine particles of sand, mud, and organic matter in suspension, and some of this is deposited onto the sea bed. The length of the pipeline is such that the concentration of deposited activity on the sea shore is about 50 times lower than that on the sea bed near the effluent outlet. The fish in this area, of which plaice are the most important, live on the sea bed and consequently take up activity from the water, from the particles, and from the invertebrates which form their food. The activity level in the edible parts of fish is many hundred times less than that in the sea bed sand and is probably not greatly different from that of the surrounding water. Some of the activity reaching the shore is absorbed not by the sand but by seaweed, and, since this weed is used almost directly as a food, stringent limits have had to be placed on its activity. Most of the weed harvested in Cumberland grows within about 20 kilometers of the effluent outlet, and there is no substantial dilution by weed from other areas. Consequently, maximum permissible discharges are limited primarily by the activity of this weed and by the need to safeguard the small group of people (the Welsh) who regularly eat it in quantity.

The results of this experimental program have shown that it would be safe to release some 15,000 curies per month of fission products at a point about 3 kilometers off this part of Cumberland coast. Further work now in hand suggests that this figure could reasonably be increased to over 45,000 curies per month. These high figures are possible because the



marine processes in this area cause sufficient dispersal to prevent any continuing build-up from year to year of the activity levels either in the vicinity of the outlet or in the more widespread regions of the Irish Sea.

### Adsorption of Activity on Natural Materials

Radioactive waste and ground water solutions were passed through columns of indigenous Conasauga shale to determine the sorptive behavior of the radionuclides.<sup>4</sup>  $\text{Cs}^{137}$ , the major radioactive constituent of the basic waste solution, was adsorbed very effectively with a shale to solution distribution ratio of 500.

Ruthenium and the small amounts of  $\text{Co}^{60}$  and  $\text{Sb}^{125}$  present were removed by coprecipitation with lead dioxide after the addition of sodium hypochlorite. By combining coprecipitation with adsorption on shale columns, it was possible to obtain decontamination factors of  $2 \times 10^3$  for gross beta,  $3 \times 10^3$  for gross gamma,  $4 \times 10^4$  for cesium, and  $2 \times 10^2$  for ruthenium.

In studies of clay columns<sup>5</sup> for the absorption of activity from radioactive wastes, static experiments on the effect of gamma irradiation showed no adverse effects at levels up to  $10^7$  R. With levels up to  $5 \times 10^8$  R, the individual clay rods were intact but some gas pockets had formed in the interstices. Two of the three columns in the  $10^8$  R group have been put on stream with simulated waste solutions and appear to be operating satisfactorily.

Ninety per cent of the  $\text{Sr}^{90}$  discharged to two abandoned cribs at Hanford was accounted for in a cylinder of soil of approximately about 120 to 140 ft in diameter and 30 ft deep.<sup>6</sup> The audit of  $\text{Sr}^{90}$  was calculated using the radioanalysis of soil samples taken from wells located near the circumference of the cylinder. In nearly all these soil samples,  $\text{Cs}^{137}$  was not detectable which prohibited making a  $\text{Cs}^{137}$  audit. The absence of  $\text{Cs}^{137}$  is evidence that it was removed by the soil before the waste reached the wells. The material balance of long half-life isotopes or "positive" approach method of auditing of wastes discharged to the ground appears to be a feasible reinforcement to the

present monitoring method. However, it would be very expensive, requiring a large number of isotopic analyses of the influent to a crib and possibly tripling the number of wells required within the crib.

### Isotope Production

This subject was included in the last Review for the purpose of noting some information from the USSR. It is reported this time to present some information on Polish plans in this field.<sup>7</sup> One of the functions of the 2-Mw research reactor (fuel, 10 per cent enriched uranium; flux,  $2 \times 10^{13}$  neutrons/(sq cm)(sec); moderator and coolant, water) to be started up in a near future will be a limited production of radioisotopes for medical, biological, and radiochemical applications. They will be prepared to handle samples containing up to 10 curies of beta activity and 2 curies of gamma activity. The isotopes which will be made available are:  $\text{Co}^{60}$ ,  $\text{Ir}^{192}$ ,  $\text{Tl}^{204}$ ,  $\text{Tm}^{170}$ ,  $\text{Au}^{198}$ ,  $\text{I}^{131}$ ,  $\text{P}^{32}$ ,  $\text{S}^{35}$ ,  $\text{C}^{14}$ , and tritium.

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## CONVERSION OPERATIONS TO FINAL PRODUCTS

The production of uranium and thorium metals is an important part of the fuel cycle for those reactors which utilize metallic fuels. New developments in the field of metal production are reviewed in this section. The fuel cycle for enriched uranium necessarily involves conversions to and from the compound uranium hexafluoride (used in the gaseous-diffusion process). New developments in processing uranium hexafluoride are also reviewed herein.

### *Reduction of $UF_6$ with Hydrogen*

A dry process for the reduction of uranium hexafluoride to uranium tetrafluoride by reaction with hydrogen gas has been developed. A pilot plant was installed and operated at the Oak Ridge Gaseous Diffusion Plant to evaluate operational problems which might be encountered in a plant of this type. An operating manual for the pilot plant was recently issued,<sup>1</sup> and process development studies have been described in earlier reports.<sup>2,3</sup>

In the reaction of uranium hexafluoride with hydrogen to produce uranium tetrafluoride and hydrogen fluoride, the thermodynamic equilibrium is considerably toward the formation of uranium tetrafluoride; however, a high activation energy is required to initiate and sustain the reduction process. The continuous addition of a controlled amount of fluorine to the uranium hexafluoride feed stream supplies the required energy by burning with hydrogen. The fluorine addition has the added advantages of controlling the density of the uranium tetrafluoride product and preventing the formation of solid intermediate uranium fluorides, e.g.,  $UF_5$ ,  $U_2F_7$ , and  $U_3F_{10}$ , which tend to fuse under operating conditions and stick to the reactor wall.

The reduction reaction is carried out in a monel vertical pipe reactor. The reactants, a uranium hexafluoride-fluorine mixture and hydrogen, are supplied to the reactor through a concentric nozzle assembly in the reactor head flange. The uranium hexafluoride-fluorine mixture flows through the inner tube of the nozzle,

while the hydrogen flows through the annulus. Nozzle velocities are approximately 50 ft/sec to prevent back diffusion and to ensure turbulent mixing of the reactant gases in the reaction zone. The reaction occurs in a narrow incandescent flame envelope below the nozzle tip.

The reaction product, uranium tetrafluoride powder, is swept toward the bottom of the reactor by the by-product, anhydrous hydrogen fluoride, and the excess hydrogen. About 90 per cent of the uranium tetrafluoride powder settles out in a hopper at the base of the reactor as the gas phase reverses direction and passes upward through a 30-deg angled leg of the gas-solids separation section. The remaining gas-entrained solids are separated from the carrier gas by a mechanical filter in the reactor outlet arm. Powder accumulations on the filter element are dislodged by vibration and fall by gravity into the product hopper-receiver. The filtered off-gases pass through a second mechanical filter which ensures against product loss if the first filter becomes damaged.

Before disposal, the waste gas is scrubbed free of unreduced uranium hexafluoride in calcium sulfate chemical traps. Normally, the reactor off-gases contain 8 to 10 ppm of uranium hexafluoride. The mechanically and chemically filtered waste gas is then discharged into a water scrubber which strips hydrogen fluoride from the gas mixture. The remaining gas is discharged to the atmosphere.

After completion of development work on the process, an extended test of the pilot-plant unit was made. The uranium tetrafluoride product was of good quality and had an average top density of 3.0 g/cc. A complete uranium balance was maintained, and no measurable loss occurred. Equipment performance, in general, was good.

### *Preparation of U Metal by*

#### *Carbothermic Reduction of $UO_2$*

Uranium oxide has been reduced by carbon under vacuum at 2250°C to yield a product con-

sisting of dendritic uranium carbide in a matrix of uranium.<sup>4</sup> Uranium sponge is obtained from this cermet by hydrolyzing the interconnected uranium carbide. This is followed by pickling in dilute nitric acid to remove the residual hydrolysis product, uranium dioxide, from the metal. The end product of this process is a uranium metal sponge of exceptionally high purity, well within the stringent specifications required for reactor use.

As carried out on a 100-lb scale, the average over-all yield of uranium from 21 reduction runs was 31.2 per cent per reduction cycle. The remaining uranium is in the form of hydrolysis product ( $\text{UO}_2$ ) and leach product (uranyl nitrate solution) which require recycling.

This reduction process has the advantage of requiring less expensive raw materials than those employed at present. Thus uranium dioxide is used rather than the more expensive uranium tetrafluoride, and carbon is used rather than magnesium. The product is in the form of bright sponge which lends itself readily to further treatment, such as arc-melting to pure metal or alloys or direct fuel-element fabrication by rolling. The considerable losses that occur when a uranium ingot is remelted, scalped, and/or machined or rolled to size for fuel elements are avoided.

Disadvantages of the process lie in the high temperatures involved, the crucible attrition, the low yields of metal per reduction cycle (30 to 45 per cent to date), and in the necessity for consolidating the bright sponge under an inert atmosphere soon after its final pickling and drying.

Large-scale reductions were carried out in a 4-ft-diameter stainless-steel vacuum shell equipped with an internal induction coil, view ports, and a high-capacity pumping system. Feed in the form of pelletized uranium dioxide-carbon mixtures was loaded into a crucible in the furnace. As the mixture of  $\text{UO}_2$  and carbon was heated under vacuum, carbon monoxide was evolved. At the maximum temperature, 2200°C, the oxygen-free charge fused into a "biscuit" of uranium metal and uranium carbide. The average metal content of the biscuit was 40 per cent, as determined by density measurements.

Graphite has been found to be the most suitable material for the reduction crucible in spite of its rapid reaction at 2200°C with the

uranium to form the carbide. No refractory oxide or carbide has been found that is unreactive to the molten charge at these high temperatures.

The uranium carbide is removed by hydrolysis of the biscuit in warm water. This leaves surface-oxidized sponge metal, which is pickled in dilute nitric acid to remove oxide. The average per cent metal recovery from leaching was 88.6 per cent.

The high-purity uranium sponge produced in the carbothermic reduction process makes a unique material for fuel-element fabrication. The sponge may be clad and rolled to give a fuel element of any degree of porosity. Small rounded porous pellets can be made by hammer milling in an argon atmosphere. Because of its extensive surface area the sponge may be readily hydrided and compacted by powder metallurgical techniques. The oxide resulting from hydrolysis might be useful in fuel slurries because of its extremely fine particle size.

### *Production of Th Metal*

#### *by Calcium Reduction of $\text{ThO}_2$*

A process for the production of high-purity thorium metal powder by direct calcium reduction of thorium oxide has been developed.<sup>5</sup> The process has evolved from small-scale experiments on 200-g batches and is now capable of producing 11-lb batches of powder. Since high-purity calcium is now available commercially at a low cost, the method shows promise of becoming an economically practical one for producing thorium metal of reactor quality.

The raw thorium oxide, after a calcining operation to remove carbon, is blended with calcium chloride and calcium metal in about 25 per cent excess. The blended charge is fired to 950°C in a tapered, type 446 stainless-steel reactor to effect complete reduction. The reduction product is jolted out of the reactor, crushed to suitable particle size in a jaw crusher, and leached with water. The resulting powder is washed with additional water and with dilute nitric acid to remove all the calcium. The wet powder is then dried by washing with organic solvents, acetone and petroleum ether, to displace water.

The calcium hydroxide and nitric acid suspensions from the washing operations contain

10 to 15 per cent of the thorium powder as fines. These fines may be recovered and recycled through the reduction step.

Thorium powder prepared in this process has been consolidated by (1) consumable electrode arc-melting, (2) hot compaction, and (3) cold compaction and sintering. The first of these methods produces fully dense metal of the highest purity.

On the present scale of production, yields of thorium powder as high as 91 per cent of the theoretical have been attained. If the fines separated during the washing operations were included, the yield of powder would exceed 99 per cent since the conversion of oxide to metal is essentially complete.

The initial calcining operation on the thorium oxide raw material removes carbon dioxide adsorbed from the air and decomposes any residual oxalate in the thorium oxide. The addition of calcium chloride to the charge is required to provide a fluid medium for contact between the reactants. The use of high-purity redistilled calcium metal is essential for good quality product. The reduction is carried out under a flow of argon to eliminate gaseous contaminants.

### *Production of Th Metal by Sodium Vapor Reduction*

The vapor phase, high-temperature sodium reduction of thorium tetrachloride has been investigated on a bench scale.<sup>6</sup> Sublimed thorium tetrachloride carried in a stream of mercury vapor was contacted with sodium vapor, diluted with helium. The apparatus contained two vaporizers for converting the thorium salt and the sodium into gases which passed into a reactor consisting of an 18-in. horizontal section of 4-in.-diameter stainless-steel pipe. An air-cooled condenser was connected to the exit end of the reactor.

The products when cooled were noted to consist of nearly equal amounts of a solid powder phase and a phase which appeared to be clean mercury. Thorium, sodium, and chloride were found predominantly in the powder phase. Examination of the powder phase revealed that it was composed of small mercury drops which were prevented from coalescing by a film of powder. The unreacted sodium and soluble salts were removed by water washing, and the

insoluble powder was separated. The yield of the product powder was not determined since complete separation was impossible. However, indirect evidence indicated that a large fraction of the thorium in the product was reduced to the metallic state. Moderate corrosion of the type 347 stainless steel apparatus was noted during the experimental work.

Although the results of the experimental investigation do not permit any immediate industrial utilization of the process, the preliminary work may serve to encourage further study of this novel technology.

### *New Plant for Reactor Feed Materials*

A new privately owned plant for production of uranium and thorium oxides, salts, or metals<sup>7</sup> has been put into operation by Davison Chemical Company at Erwin, Tenn. The plant takes thorium or uranium concentrates, scrap, or enriched uranium hexafluoride and converts these into finished forms.

Two methods for uranium processing are used. In the first method, uranium hexafluoride is converted to uranium tetrafluoride by reaction with hydrogen. This is reacted with steam to produce uranium dioxide or is reacted with magnesium or calcium to produce uranium metal. In the second method, the uranium hexafluoride is dissolved in water and precipitated as ammonium diuranate, which can be decomposed to produce uranium oxide.

In the thorium process, thorium concentrate is digested in acid, and the thorium is solvent extracted in pulse columns. Thorium is then precipitated as thorium oxalate, which is decomposed by heat to thorium oxide. The oxide can be reacted with calcium to provide thorium metal or sintered into dense compacts after being blended with uranium oxide.

The plant is equipped to produce uranium or thorium ingots, either pure or alloyed. The metal can be rolled or extruded and assembled into finished fuel elements.

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